



**US Army Corps
of Engineers**

Engineer Research and
Development Center

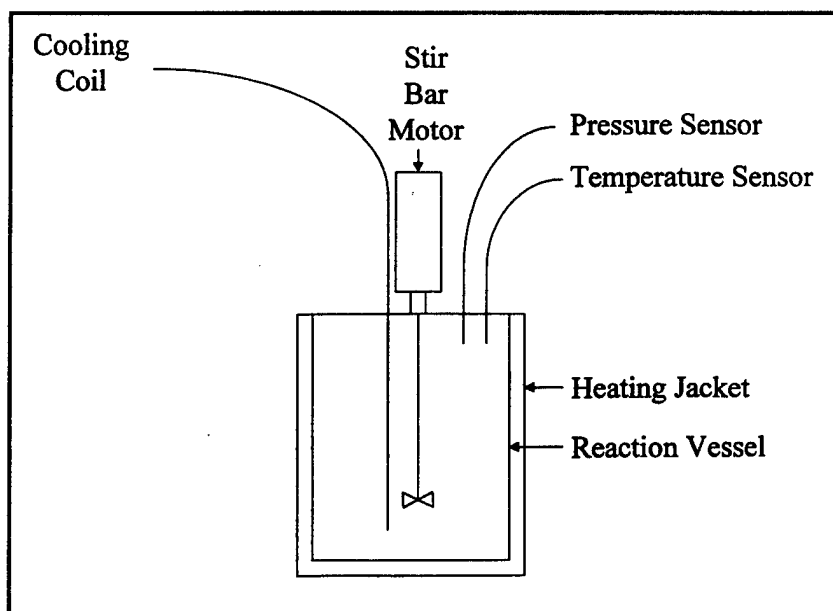
CERL Technical Report 99/74
September 1999

Reuse of Ammonium Nitrate

Wet Air Oxidation

Stephen W. Maloney

Ammonium nitrate (AN) is a possible replacement for ammonium perchlorate as an oxidizer in solid rocket motors potentially generating large amounts of AN to be recycled or reused. AN requires phase stabilization before it can be used, so small amounts of potassium dinitrimide (KDN) are added to create phase stabilized ammonium nitrate (PSAN). Reuse alternatives would either require separating the KDN or destroying it. AN is commonly used as a fertilizer (80 percent of AN produced) and an oxidizer. Owing to the high demand and wide availability of AN for its most common use, the commercial cost is very low. This precludes reuse alternatives, which would require separation of the KDN. So, this report focused on destructive reuse as an oxidizer in wet air oxidation (WAO). The PSAN was tested to see if KDN was destroyed during WAO, and AN was tested as an oxidizer in WAO treatment of an Army hazardous waste sludge. WAO will degrade KDN, and PSAN can be effectively used as an oxidizing agent. The hazardous waste sludge could be treated effectively. Sludge volume index was significantly reduced, meaning that the amount of sludge requiring disposal would be greatly reduced, offsetting the cost of WAO.



20000306 049

DTIC QUALITY INSPECTED 3

Foreword

This study was conducted for the Directorate of Research and Development, Headquarters, U.S. Army Corps of Engineers (HQUSACE) under Project 4A16270D048, "Industrial Operations Pollution Control Technology"; Work Unit T77, "Reuse of Waste Ammonium Nitrate." The Technical Monitor was Richard Eichholtz, SFIM-AEC-ET.

The work was performed by the Environmental Processes Branch (CN-E) of the Installations Division (CN), U.S. Army Construction Engineering Research Laboratory (CERL). The CERL Principal Investigator was Dr. Stephen W. Maloney and the technical editor was Debra K. Krites, Information Technology Laboratory - Champaign. Dr. Ilker R. Adiguzel is Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The Acting Director of CERL is Dr. Alan W. Moore.

CERL is an element of the Engineer Research and Development Center (ERDC), U.S. Army Corps of Engineers. The Acting Director of ERDC is Dr. Lewis E. Link, Jr., and the Commander is COL Robin R. Cababa, EN.

DISCLAIMER

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products. All product names and trademarks cited are the property of their respective owners.

The findings of this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

DESTROY THIS REPORT WHEN IT IS NO LONGER NEEDED. DO NOT RETURN IT TO THE ORIGINATOR.

Executive Summary

Ammonium nitrate (AN) has been under consideration as a replacement for ammonium perchlorate as an oxidizer in solid rocket motors. This potentially could generate large amounts of AN to be recycled or reused.

AN requires phase stabilization before it can be used in solid rocket motors. To accomplish this, small amounts of potassium dinitrimide (KDN) are added to the mix, to create phase stabilized ammonium nitrate (PSAN). Reuse alternatives would either require separation of the KDN, or must result in the destruction of KDN.

An on-line search of the Chemical Abstracts and National Technical Information Services (NTIS) databases for common uses of AN confirmed its use as a fertilizer (80 percent of AN produced) and an oxidizer. A number of other supplemental uses were also identified. They are:

- Peacetime explosives: e.g., rock blasting
- Propellants: air bags, fire extinguishers, life vests
- Chemical processes: chemical preparation, separation, analysis
- Coating metals: plating, cladding, anodizing
- Cooling/heating agents: chemical refrigerants, melting ice.

An economic evaluation was carried out to determine the potential cost of reuse. Owing to the high demand and wide availability of AN for its most common use, the commercial cost is very low. This precludes reuse alternatives, which would require separation of the KDN. For that reason, this report focused on destructive reuse as an oxidizer in wet air oxidation (WAO). The PSAN was tested for destruction of KDN during WAO, and AN was tested as an oxidizer in WAO treatment of an Army hazardous waste sludge.

The results indicate that WAO will degrade KDN, and that PSAN can be effectively used as an oxidizing agent in WAO. Nitrous oxide (N_2O) was found to be a significant by-product in the offgas of the treatment when KDN was present in the feed stream. WAO tests with a hazardous waste sludge from munitions production indicated that it could be treated effectively, but that a by-product was

formed, which condensed on the cooling coils and also condensed as a gel in the effluent. This by-product was avoided when the temperature of WAO was maintained at 325 °C. A secondary effect was a major reduction in the sludge volume index, which means that the amount of sludge requiring disposal as a hazardous waste would be greatly reduced, which would offset the cost of WAO.

Contents

Foreword	2
Executive Summary	3
List of Figures and Tables	7
1 Introduction	9
Background	9
Objectives	9
Approach	9
Scope	10
Mode of Technology Transfer	10
Metric Conversion Factors	10
2 Economic Comparison of Reuse Alternatives	11
Base Cost Development	11
Reuse Options	11
Separation and Recovery of AN from KDN for Use as Fertilizer	11
<i>Reuse Of AN As Fertilizer</i>	<i>12</i>
<i>Reuse As an Oxidizer in Wet Air Oxidation</i>	<i>12</i>
Economic Comparison of Reuse Alternatives Summary	13
3 Wet Air Oxidation Testing	15
Construction Materials for WAO System	18
Experimental Procedures	18
<i>Analytical Procedures</i>	<i>18</i>
<i>Shaking Autoclave Procedures</i>	<i>19</i>
Procedures for Testing Construction Materials	19
Results and Discussion	20
<i>AN Testing</i>	<i>20</i>
<i>KDN Testing</i>	<i>26</i>
<i>AN + KDN Solutions—Simulated PSAN</i>	<i>32</i>

Results of Testing Potential WAO System Construction Materials	37
<i>AN + Phenol</i>	39
<i>KDN + Phenol</i>	39
<i>AN + KDN + Phenol</i>	40
4 Wet Air Oxidation of Hazardous Waste Sludge	41
5 Summary	50
References	51
Appendix A: Cost Calculation for Reuse Alternatives	53
Appendix B: Calculations for Shaking Autoclave Tests	57
Appendix C: WAO and RAAP Sludge — Final Water Quality Data	95
Distribution	96
Report Documentation Page	97

List of Figures and Tables

Figures

1	Shaking autoclave	19
2	Material test coupon	38
3	Wet air oxidation reactor	42
4	COD remaining vs. temperature — 150 mL sludge + 100 mL AN	44
5	TSS remaining vs. temperature — 150 mL sludge + 100 mL AN	45
6	SVI vs. temperature — 150 mL sludge + 100 mL AN	45
7	COD reduction vs. temperature — 170 mL sludge + 80 mL AN	46
8	TSS reduction vs. temperature — 170 mL sludge + 80 mL AN	46
9	SVI vs. temperature — 170 mL sludge + 80 mL AN	47
10	COD reduction vs. temperature — 190 mL sludge + 60 mL AN	47
11	TSS reduction vs. temperature — 190 mL sludge + 60 mL AN	48
12	SVI vs. temperature — 190 mL sludge + 60 mL AN	48

Tables

1	List prices for ammonium nitrate	11
2	Unit costs per pound of ammonium nitrate processed	13
3	Test conditions for the oxidation with AN	16
4	Test conditions for the oxidation with KDN	16
5	Test conditions for the oxidation with AN + KDN	17
6	Wet air oxidation results — AN, 5 g/L	21
7	Wet air oxidation results — AN, 5 g/L + phenol, 500 mg/L	22
8	Wet air oxidation results — AN, 5 g/L + acetic acid, 1,000 mg/L	24
9	Wet air oxidation results — AN, 5 g/L + biosludge	25
10	Wet air oxidation results — KDN, 10 g/L	27
11	Wet air oxidation results — KDN, 10 g/L + phenol, 500 mg/L	28
12	Wet air oxidation results — KDN, 10 g/L + acetic acid, 1 g/L	30
13	Wet air oxidation results — KDN, 10 g/L + biosludge	31
14	Wet air oxidation results — AN, 5 g/L + KDN, 10 g/L	33
15	Wet air oxidation results — AN, 5 g/L + KDN, 10 g/L + phenol, 1,000 mg/L	34
16	Wet air oxidation results — AN, 5 g/L + KDN, 10 g/L + acetic acid, 2 g/L	35
17	Wet air oxidation results — AN, 5 g/L + KDN, 10 g/L + biosludge	37
18	Composition of evaluated materials	38
19	Materials of construction testing results	39

20	Materials of construction testing results	40
21	Materials of construction testing results	40
22	RAAP aerobic digester sludge characteristics	41
23	Summary of RAAP sludge experimental conditions	43
A-1	Separation of Ammonium Nitrate (AN) From Potassium Dinitrimide (KDN) Using Reverse Osmosis	54
A-2	Reuse of Pure Ammonium Nitrate (AN) as Fertilizer	55
A-3	Use of Ammonium Nitrate (AN) as an Oxidizer in Wet Air Oxidation	56

1 Introduction

Background

The motors of large rockets currently use ammonium perchlorate as one of the major components of their propellant. The ammonium perchlorate generates large amounts of chloride as it burns, which contributes to acid rain and structural damage through corrosion at launch facilities. As a result, the Army is considering replacement of the ammonium perchlorate with ammonium nitrate. This would avoid environmental problems attributed directly to the chloride production.

Ammonium nitrate (AN) is an explosive and oxidizer that has been used in many applications requiring energetic materials. However, it has caused problems when directly used in rocket motors, and requires a stabilizing agent: potassium dinitrimide (KDN). The resulting material is called phase stabilized ammonium nitrate (PSAN). Rocket motors containing PSAN are not currently available. If they were produced, however, potentially large quantities of PSAN could be generated as a by-product from building and demilitarizing them.

Objectives

The overall objective of this study was to determine if there were economic reuse alternatives for PSAN, and what the cost or potential savings would be from its use. Three subobjectives have been addressed to meet the overall objective. They are (1) an economic and market analysis to establish a base price for commercial AN, (2) an analysis of a technology to destroy KDN, wet air oxidation (WAO), and (3) an analysis of WAO of a typical Army hazardous waste sludge.

Approach

An economic analysis of the market cost of AN was conducted by contacting typical manufacturers (DSM Chemicals, Augusta, GA, and LaRoche Industries, Atlanta, GA) and by using *Green Markets Price Scan* (Price and Fischer, no date). This was used as a baseline to compare the cost of removing KDN from PSAN to purchasing AN on the

open market. This would allow an estimate of the potential for savings to be derived from selling the purified AN.

A destructive technique using WAO was then analyzed for its ability to degrade the KDN. The benefit of using PSAN in this method is providing an oxidant for the degradation of organics. WAO is typically applied to sludges and high strength wastewaters that require large quantities of oxidant.

An actual Army hazardous waste sludge was also treated, using WAO with AN as the oxidizer. This was added to the work after tests determined that KDN was destroyed by WAO, giving further information on the destruction of the sludge, and on by-products. Co-disposal of the PSAN with hazardous waste sludge could offset the cost of WAO by reducing the amount of sludge produced.

Scope

The techniques described and evaluated in this report apply to Army industrial activities. The agencies responsible for development and treatment of propellants in rocket motors will benefit from the information presented here, and it will allow them to estimate the cost and requirements for disposal of waste from rocket motors containing PSAN.

Mode of Technology Transfer

The findings and recommendations in this report should be used as a foundation for developing and testing reuse and disposal alternatives in the development of a new generation of rocket motors.

Metric Conversion Factors

The following metric conversion factors are provided for the standard units of measure used throughout this report.

1 lb	=	0.453 kg
1 in.	=	25.4 mm
1 ton	=	907.7 kg
1 gal.	=	3.78 L
1 cu ft	=	0.03 m ³
1 acre	=	4,046.9 m ²
1 psi	=	6,894.8 Pa

2 Economic Comparison of Reuse Alternatives

Base Cost Development

An on-line search of the Chemical Abstracts and National Technical Information Services (NTIS) databases for common uses of AN confirmed its use as a fertilizer (80 percent of AN produced) and an oxidizer. A number of other supplemental uses were also identified. They are:

- Peacetime explosives: e.g., rock blasting
- Propellants: air bags, fire extinguishers, life vests
- Chemical processes: chemicals preparation, separation, analysis
- Coating metals: plating, cladding, anodizing
- Cooling/heating agents: chemical refrigerants, melting ice.

Several sources of AN price information were consulted, as summarized in Table 1.

Reuse Options

Two reuse options for AN were evaluated in this study: as fertilizer and as an oxidizer chemical in WAO. Both options may also be considered disposal alternatives for AN as part of the demilitarization of munitions containing this compound.

Separation and Recovery of AN from KDN for Use as Fertilizer

To develop a cost per pound for recovering AN, a 10 gal/min basis for a reverse osmosis (RO) system was established. An average concentration of 10 percent by weight AN and a slurry density that is 8 percent greater than water were assumed. The

Table 1. List prices for ammonium nitrate.

Source	Cost (\$/ton)	Cost (\$/lb)
PCS Nitrogen (DSM Chemicals)	185	0.093
LaRoche Industries	165	0.083
Green Markets Price Scan	135-205	0.068-0.103

costs for necessary system components were estimated, with assistance from the Purification Products Corporation. Representatives of this firm felt that the desired separation may work, but that there would likely be a very high rejection rate for all solutes (ammonia, nitrate, and KDN); a pilot study is required to work out the operational details of using RO. They also said that ultrafiltration would probably not work at all in this application owing to the size of molecules and their similarity.

The estimated cost of implementing this option is presented in Table A-1 in Appendix A. The amount of AN to be processed in 1 year is:

$$10 \text{ (gal/min)} \times 60 \text{ (min/hr)} \times 8 \text{ (hr/day)} \times 5 \text{ (day/wk)} \times 52 \text{ (wk/year)} \times [(1/7.4805) \times (\text{ft}^3/\text{gal})] \times 62.4 \text{ (lb/ft}^3) \times 1.08 \times 0.1 \text{ (lb AN/1.0 lb slurry)} = 1,124,326 \text{ (lb AN/year)}$$

The unit cost, based on Table A-1, is therefore \$0.60/lb of AN. All unit costs are based on an amortized capital cost at 7 percent over a 10-year period. This is added to the annual operation and maintenance (O&M) cost, and then divided by the through-put for the system.

Reuse Of AN As Fertilizer

To develop a cost per pound for using AN in this way, a basis of 10 acres requiring fertilization was established. The costs associated with this option are estimated in Table A-2. This use is analogous to the site fertilization conditions presented for ex-situ land farming in the *Environmental Cost Handling Options and Solutions (ECHOS) Handbook* (Means 1997). The *Handbook* recommends using 800 lb of AN per acre. The unit cost, based on Table A-2, is \$5.26/lb of AN $[(17,765 + 24,350)/8,000] = 5.26$; this may also be considered a disposal cost if there is no market for reprocessed AN from rocket motors. The cost is increased further when the recovery process described above is added to account for pure AN being required. This adds \$0.60 to the cost for a total of \$5.86/lb of AN.

Reuse As an Oxidizer in Wet Air Oxidation

AN may be used successfully as an oxidizing agent in the WAO process. Tests of this application are described in the following sections of this report. The presence of KDN is not known to interfere with the effective use of AN in this application.

To develop a cost per pound for using AN in WAO, a 2 gal/min basis was established for a fully equipped WAO system. An average concentration of 10 percent by weight AN and a slurry density that is 8 percent greater than water were assumed. The estimate of costs associated with this option are summarized in Table A-3. The estimated amount of AN to be processed in a year is:

$$2 \text{ (gal/min)} \times 60 \text{ (min/hr)} \times 8 \text{ (hr/day)} \times 5 \text{ (day/wk)} \times 52 \text{ (wk/year)} \times [(1/7.4805) \text{ (ft}^3\text{/gal)}] \times 62.4 \text{ (lb/ft}^3\text{)} \times 1.08 \times 0.1 \text{ (lb AN/1.0 lb slurry)} = 224,865 \text{ (lb AN/year)}$$

The unit cost, based on Table A-3, is therefore \$1.57/lb of AN; this may also be considered a disposal cost.

Economic Comparison of Reuse Alternatives Summary

The unit costs of reuse options for PSAN were estimated and compared with the present baseline cost for AN from commercial suppliers (Table 2). These costs are based on prospective recovery methods to estimate the potential for recovery and reuse to compete economically with the existing supply of AN.

The value shown for WAO is a disposal cost. AN has been successfully used as an oxidizing agent in this process, reducing the amount of air or oxygen required for treating a batch of waste-slurry materials.

Discussions with ultrafiltration equipment suppliers indicate that separation of AN from KDN would not be feasible; RO was recommended. The estimated cost given for the separation and recovery option represents capital and O&M costs for a process with a capacity of 10 gal/min. This system uses RO membranes and an evaporator/crystallizer to separate the AN from the KDN stabilizer. This produces AN suitable for use as fertilizer. However, RO membranes are expected to have a relatively high rejection rate in this application, and establishing the effectiveness of the degree of separation from the stabilizer will require laboratory tests.

These results show that none of the reuse options are currently competitive with the relatively low price of AN available commercially. Some of the key economic factors that contribute to this result are:

Table 2. Unit costs per pound of ammonium nitrate processed.

Option	Cost (\$/lb)
Wet air oxidation	1.57
Separation/recovery	0.60
Use pure AN as fertilizer	5.26
Use as fertilizer, after recovery	5.86
AN (commercial)	0.068–0.103

- The consistently low price of AN on the open market, as it is produced in large quantities by mature, well-established production processes.
- The lack of efficiency in recovery methods, which often require grinding or pulverizing the propellant material, mixing it in a slurry for separation, then reconstituting the wet, concentrated AN into a solid by evaporation and crystallization.

The remainder of this report will focus on WAO as the disposal method since reprocessed AN cannot compete with commercially produced AN.

3 Wet Air Oxidation Testing

WAO was tested with solutions of AN, KDN, and a mixture of AN + KDN. There currently is no production waste from AN-based rocket motors, so the actual composition of the wastewater, and the ratio of AN to KDN, is unknown. Therefore, this is simulated PSAN wastewater. To determine the oxidation potential of these various solutions, an organic substrate was added to some of the autoclave tests. The study involved 36 different autoclave oxidations, using various solutions and oxidation temperatures. The experiments included:

- AN testing
 - Three autoclave oxidations using 5 g/L AN
 - Three autoclave oxidations using 5 g/L AN + 500 mg/L phenol
 - Three autoclave oxidations using 5 g/L AN + 1,000 mg/L acetic acid
 - Three autoclave oxidations using 5 g/L AN + biosludge.
- KDN testing
 - Three autoclave oxidations using 10 g/L KDN
 - Three autoclave oxidations using 10 g/L KDN + 500 mg/L phenol
 - Three autoclave oxidations using 10 g/L KDN + 1,000 mg/L acetic acid
 - Three autoclave oxidations using 10 g/L KDN + biosludge.
- AN + KDN testing
 - Three autoclave oxidations using 5 g/L AN + 10 g/L KDN
 - Three autoclave oxidations using 5 g/L AN + 10 g/L KDN + 1,000 mg/L phenol
 - Three autoclave oxidations using 5 g/L AN + 10 g/L KDN + 2,000 mg/L acetic acid
 - Three autoclave oxidations using 5 g/L AN + 10 g/L KDN + biosludge.

Tables 3, 4, and 5 list the autoclave oxidations. The various WAO temperatures (260, 280, and 300 °C) were investigated to evaluate the operating temperature at which the treatment objectives would be best achieved.

The test solutions were prepared in distilled water. The AN, phenol, and acetic acid were purchased from Aldrich Chemical Company. All of the chemicals added were soluble. With the exception of the biosludge samples, the solutions were free of sus-

Table 3. Test conditions for the oxidation with AN.

Autoclave Run Number	Oxidation Solution	Oxidation Temperature (°C)	Residence Time, Minutes
1	AN, 5g/L	260	60
2	AN, 5g/L	280	60
3	AN, 5g/L	300	60
3a	AN, 5g/L + Copper	280	60
4	AN, 5g/L+Phenol 500 mg/L	260	60
5	AN, 5g/L+Phenol 500 mg/L	280	60
6	AN, 5g/L+Phenol 500 mg/L	300	60
7	AN, 5g/L+Acetic Acid 1g/L	260	60
8	AN, 5g/L+Acetic Acid 1g/L	280	60
9	AN, 5g/L+Acetic Acid 1g/L	300	60
10	AN, 5g/L+Biosludge	260	60
11	AN, 5g/L+Biosludge	280	60
12	AN, 5g/L+Biosludge	300	60

Table 4. Test conditions for the oxidation with KDN.

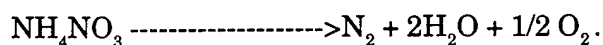
Autoclave Run Number	Oxidation Solution	Oxidation Temperature (°C)	Residence Time, Minutes
13	KDN, 10g/L	260	60
14	KDN, 10g/L	280	60
15	KDN, 10g/L	300	60
15a	KDN, 10g/L+copper	280	60
16	KDN, 10g/L+phenol 500 mg/L	260	60
17	KDN, 10g/L+phenol 500 mg/L	280	60
18	KDN, 10g/L+phenol 500 mg/L	300	60
19	KDN, 10g/L+acetic Acid 1g/L	260	60
20	KDN, 10g/L+acetic Acid 1g/L	280	60
21	KDN, 10g/L+acetic Acid 1g/L	300	60
22	KDN, 10g/L+biosludge	260	60
23	KDN, 10g/L+biosludge	280	60
24	KDN, 10g/L+biosludge	300	60

Table 5. Test conditions for the oxidation with AN + KDN.

Autoclave Run Number	Oxidation Solution	Oxidation Temperature (°C)	Residence Time, Minutes
25	AN, 5g/L + KDN, 10g/L	260	60
26	AN, 5g/L + KDN, 10g/L	280	60
27	AN, 5g/L + KDN, 10g/L	300	60
28	AN, 5g/L + KDN, 10g/L + Phenol 1000 mg/L	260	60
29	AN, 5g/L + KDN, 10g/L + Phenol 1000 mg/L	280	60
30	AN, 5g/L + KDN, 10g/L + Phenol 1000 mg/L	300	60
31	AN, 5g/L + KDN, 10g/L + Acetic Acid 2g/L	260	60
32	AN, 5g/L + KDN, 10g/L + Acetic Acid 2g/L	280	60
33	AN, 5g/L + KDN, 10g/L + Acetic Acid 2g/L	300	60
34	AN, 5g/L + KDN, 10g/L + Biosludge	260	60
35	AN, 5g/L + KDN, 10g/L + Biosludge	280	60
36	AN, 5g/L + KDN, 10g/L + Biosludge	300	60

pended material and were colorless. After the solutions were mixed, the pH was adjusted to 1.0–1.3 with sulfuric acid. The biological sludge used in the testing was obtained from a secondary aeration basin at a local municipal sewage treatment plant. The biosludge samples would best be described as a concentrated mixed liquor containing volatile suspended solids.

The initial concentrations of AN and KDN were 5 and 10 g/L, respectively. These concentrations were expected to produce measurable quantities of nitrogen gas and enough oxidizing species to destroy a measurable amount of COD (chemical oxygen demand). The concentrations of phenol and acetic acid added to the solutions were based on the amount of AN and KDN added. The assumed AN decomposition reaction (reaction 1) was as follows:



The assumed KDN decomposition reaction (reaction 2) occurred in two steps as follows:



Reaction 1 indicates that for each mole of AN that decomposes, one half mole of oxygen would be released to be used as an oxidizing source. Reaction 2 also indicates that for each mole of KDN that decomposes, one half mole of oxygen would be released to be used as an oxidizing source. The concentrations of phenol, acetic acid, and biosludge added to the mixtures were expected to consume all of the oxygen produced by the above reactions. The products from the oxidations were expected to be carbon dioxide and water.

Construction Materials for WAO System

To aid in the selection of the materials to build a full-scale WAO system, five different metal alloys were evaluated for corrosion at the 300 °C test condition. Three independent material tests were performed using AN + phenol, KDN + phenol, and AN + KDN + phenol solutions. The materials were selected for testing on the basis of recommendations from previous experience of the manufacturer (Zimpro-Passavant, Rothschild, WI) in constructing WAO systems. The materials evaluated were:

- 316L Stainless Steel
- Alloy 20CB-3
- Hastelloy C-276
- Inconel 625
- Titanium grade 2.

Experimental Procedures

Analytical Procedures

All analyses included as a part of the WAO testing were performed by Zimpro's analytical laboratory, Enviroscan, according to *Standard Methods for the Examination of Water and Wastewater*, American Public Health Association, American Water Works Association, and Water Environment Federation (APHA, AWWA and WEF 1985) or *EPA Methods for Chemical Analysis of Water and Wastes* (EPA 1979).

Shaking Autoclave Procedures

All wet air oxidation tests were done in laboratory autoclaves made from titanium, each having a capacity of 500 mL. Figure 1 illustrates the shaking autoclave used in the testing. The autoclaves were charged with 250 mL of test solution and then purged with pure helium. Then they were charged with 250 psig of pure helium. The charged autoclaves were placed in a heater/shaker mechanism, heated to the desired oxidation temperature, and held for the specified reaction time. Immediately following oxidation, the autoclaves were cooled to room temperature using tap water. The pressure of the autoclave was monitored before and after the oxidation processes. The ideal gas law was used to determine the volume of gas remaining in the autoclave following the testing. After cooling, the offgas in the head space of the autoclave was analyzed for oxygen, carbon dioxide, carbon monoxide, nitrogen, total hydrocarbons (THC), nitrous oxide, and methane. Subsequent to the analyses of the offgas, the autoclave was depressurized and opened. The oxidized effluent was removed and submitted to Enviroscan for chemical analysis.

Procedures for Testing Construction Materials

Tests on the proposed WAO construction materials were performed in a titanium shaking autoclave similar to that used in the WAO testing. The tests were conducted at 300 °C for 120 hours. The test solutions were changed every 24 to 48 hours. The test coupons were welded U-bends made from commercial sheet stock of various alloys. The U-bend coupons were not annealed after welding and bending, which left

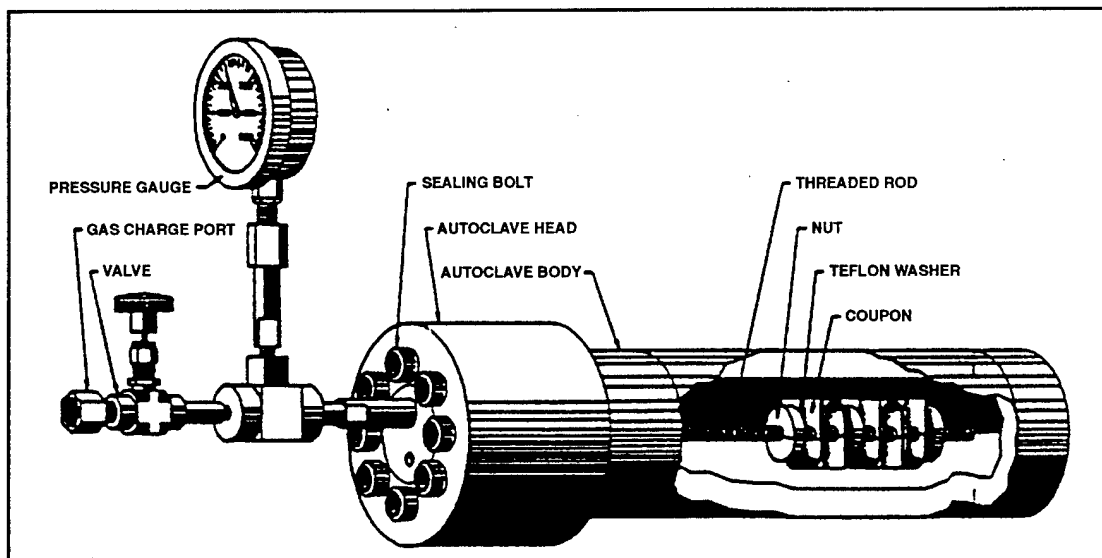


Figure 1. Shaking autoclave.

them plastically strained and residually stressed. The coupons, manufactured in accordance with ASTM G58 (ASTM 1994), were placed in the autoclave on a threaded rod and held by nuts. Teflon washers were placed between the coupons and retaining nuts to produce an area for monitoring crevice corrosion.

Before and after testing, the alloy coupons were cleaned in 10 percent nitric acid, weighed, and measured to determine a general corrosion rate. Then, after testing, they were visually and microscopically examined to assess the presence of any localized corrosion.

Results and Discussion

AN Testing

Solution with 5 g/L AN. Table 6 presents the analytical results from the WAO testing of the AN solution. The autoclave feed was not analyzed and theoretical values were used to determine the nitrogen removal efficiencies. The autoclave feed solution had a calculated total nitrogen concentration of 1,750 mg/L. The total nitrogen is calculated by adding the total Kjeldahl nitrogen (TKN) + nitrate-N + nitrite-N. The AN solution was oxidized in a helium atmosphere at three different temperatures. For this solution containing AN only, COD, nonpurgable organic carbon (NPOC), or biological oxygen demand (BOD) were not requested because none was expected in the autoclave feed.

The AN did not significantly decompose at 260 °C (run 1). The concentrations of nitrogen and nitrous oxide in the autoclave offgas were below the 0.25 volume percent detection limit. The analyses of the liquid also indicated no significant decomposition of AN. At 260 °C, the percentage of nitrogen found in the offgas was reported as 0.0 and the percentage of nitrogen removed from the liquid was 3.3. The percentage of nitrogen removed from the liquid was calculated on the basis of the theoretical nitrogen concentration in the feed compared to what remained in the oxidized effluent. The percentage of nitrogen lost in the liquid should equal the percentage of nitrogen found in the offgas. The ideal gas law was used to calculate nitrogen in the gas phase in units of milligrams of nitrogen (N) per liter of autoclave feed. The percentage of nitrogen in the offgas was determined by adding the amount of nitrogen (N₂) and nitrous oxide measured in the gas phase and comparing that value to the calculated amount of nitrogen in the autoclave feed.

As the oxidation temperature was increased to 280 and 300 °C, the decomposition of AN improved slightly; approximately 10 percent of the AN decomposed to produce

Table 6. Wet air oxidation results—AN 5 g/L.

Analyses	Feed, Calculated Concentration	AN 260 °C	AN 280 °C	AN 300 °C	AN 280 °C with Copper
Run Number	—	1	2	3	3a
An. Number	—	50023	50024	50025	50026
pH	-1.11	1.20	1.23	1.12	1.18
Nitrate- N, mg/L	875	861	792	786	685
Total Kjeldahl Nitrogen, mg/L	875	830	808	735	801
Ammonia-N, mg/L	875	830	791	767	538
Nitrite, mg/L	<0.5	<0.5	<0.5	<0.5	<0.5
N ₂ in Offgas-N, mg/L	—	0	189	101	62
N ₂ O in Offgas-N, mg/L	—	0	21	81	21
% Nitrogen in Offgas	—	0.0	10.8	10.4	4.7
% Nitrogen Removed From Liquid	—	3.3	8.6	13.1	15.1
Suspended Solids, mg/L	—	<5	<5	<5	<5
Suspended Ash, mg/L	—	<5	<5	<5	<5
Total Solids, mg/L	—	6420	6584	6364	8016
Total Ash, mg/L	—	224	472	120	2028

nitrogen gas. A good correlation was seen between the amount of nitrogen in the gas compared to the amount of nitrogen removed from the liquid. The nitrogen compounds found in the gas phase were a combination of nitrogen and nitrous oxide. No measurable concentrations of THC, CO, CO₂, or methane were detected for runs 1, 2, and 3. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

An additional oxidation was conducted with a copper catalyst in an attempt to improve the decomposition of the AN. Table 6 shows that the copper did not significantly improve its decomposition.

The data obtained indicate that AN is exceptionally resistant to decomposition when no reducing agents are present, and when the WAO condition is at or below 300 °C.

Solution with 5 g/L AN + 500 mg/L phenol. Table 7 contains the analytical results from the WAO testing of the AN + phenol solution. The autoclave feed solution had a calculated total nitrogen concentration of 1,750 mg/L and a calculated COD concentration of 1,191 mg/L. The AN + phenol solution was oxidized in a helium atmosphere at three different temperatures.

The AN significantly decomposed at 260 °C (run 4): 69 percent according to the analyses of the liquid. The percentage of nitrogen in the offgas indicated that 55 percent of the nitrogen in the autoclave feed decomposed. No measurable quantity of nitrous oxide was detected in the offgas from runs 4, 5, and 6. The destruction of COD was calculated at 90 percent for run 4. The destruction of NPOC, which would be soluble organic carbon, was measured at 87 percent.

As the oxidation temperature increased to 280 and 300 °C, the decomposition of AN improved to 86 and 87 percent, respectively, based on the loss of total nitrogen from the oxidized effluent. But, the percentage of nitrogen in the offgas points to only a 62 and 72 percent decomposition of AN at 280 and 300 °C. This imbalance between the

Table 7. Wet air oxidation results—AN, 5 g/L + phenol, 500 mg/L.

Analyses	Feed, Calculated Concentration	AN 260 °C	AN 280 °C	AN 300 °C
Run Number	—	4	5	6
An. Number	—	50027	50028	50029
COD, mg/L	1191	119	<85	<85
COD Destruction %	—	90	>93	>93
Nonpurgable Organic Carbon, mg/L	383	51	24	12
BOD	—	<60	<60	<10
pH	1.11	1.19	1.24	1.19
Nitrate- N, mg/L	875	197	76	41
Total Kjeldahl Nitrogen, mg/L	875	344	169	184
Ammonia-N mg/L	875	340	177	174
Nitrite, mg/L	<0.5	<0.5	<0.5	<0.5
N ₂ in Offgas-N, mg/L	—	965	1088	1241
N ₂ O in Offgas-N, mg/L	—	0	0	0
% Nitrogen in Offgas	—	55	62	70
% Nitrogen Removed	—	69.1	86	87

liquid and gas phases is not readily explainable. Possible sources of error would be the use of the ideal gas law and the measuring of the discharge pressure of the autoclave to determine the amount of nitrogen in the gas phase. Another source of error might be a nondetectable form of nitrogen in the gas phase and or the liquid phase.

The analytical results show a decrease in nitrate-N and ammonia-N as the oxidation temperature was increased. The concentration of nitrate-N in the oxidized effluents was not equal to the ammonia-N. Reaction 1, presented in Chapter 3, shows that the ammonia-N concentration in the oxidized effluent should equal nitrate-N. However, the analytical results say that the decomposition of AN does not completely follow reaction 1. The unexpected high level of COD destruction also means that reaction 1 is not entirely correct for predicting the decomposition of AN. At 260 °C, only 69 percent of AN decomposed, but 90 percent of COD was destroyed. The data indicate that there are more oxidizing species and more removal of nitrate than what reaction 1 predicts.

The offgas analyses indicated no formation of nitrous oxide. The concentrations of THC for runs 4, 5, and 6 varied between 22 and 27 ppm. The concentration of methane was below the 10-ppm detection limit. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

The data obtained point out that the decomposition of AN by WAO is enhanced when a reducing agent such as phenol is present. The data also suggest that low levels of nitrate-N and COD in the effluent may have inhibited complete decomposition of AN.

Solution with 5 g/L AN + 1,000 mg/L acetic acid. Table 8 contains the analytical results from the WAO testing of the AN + acetic acid solution. The autoclave feed solution had a calculated total nitrogen concentration of 1,750 mg/L and a calculated COD concentration of 1,091 mg/L. The AN + acetic acid solution was oxidized in a helium atmosphere at three different temperatures.

There was an insignificant amount of AN decomposition at 260 °C (run 7): only 4 percent, according to the analyses of the liquid. No measurable quantity of nitrous oxide was detected in the offgas from run 7; however, as the oxidation temperature increased (runs 8 and 9), a small concentration of nitrous oxide was detected. The destruction of COD was calculated at 5 percent for run 7. Acetic acid appears to be a less effective reducing agent than is phenol.

Table 8. Wet air oxidation results—AN, 5 g/L + acetic acid, 1,000 mg/L.

Analyses	Feed, Calculated Concentration	AN 260 °C	AN 280 °C	AN 300 °C
Run Number	—	7	8	9
An. Number	—	50030	50021	50022
COD, mg/L	1091	1029	850	246
COD Destruction %	—	5	22	77
Nonpurgable Organic	409	446	378	92
Carbon, mg/L	—			
BOD	—	465	411	82
BOD/COD	—	45	48	33
pH	1.11	1.19	1.23	1.19
NitMte- N, mg/L	875	860	690	117
Total Kjeldahl Nitrogen, mg/L	875	820	665	134
Ammonia-N, mg/L	875	860	695	119
Nitrite, mg/L	<0.5	<0.5	<0.5	<0.5
N ₂ in Offgas-N, mg/L	—	41	268	1173
N ₂ O in Offgas-N, mg/L	—	0	21	62
% Nitrogen in Offgas	—	.23	16.5	70.6
% Nitrogen Removed From Liquid	—	4.0	22.6	85.7
Suspended Solids, mg/L	—	<5	10	11
Suspended Ash, mg/L	—	<5	6	11
Total Solids, mg/L	—	7260	6644	6872
Total Ash, mg/L	—	2932	1760	52

As the oxidation temperature was increased to 280 and 300 °C, the decomposition of AN improved to 22 and 85 percent, respectively, based on the loss of total nitrogen from the oxidized effluent. But the percentage of nitrogen in the offgas signifies that only 16 and 70 percent of the AN decomposed at 280 and 300 °C. The imbalance in the data between the nitrogen loss in the liquid and the nitrogen produced in the gas phase is not readily explainable.

There is a good balance between expected COD destruction and AN decomposition, and a good balance between nitrate-N and ammonia-N concentrations in the oxidized effluents. These data indicate that reaction 1 closely represents the WAO process.

The concentrations of THC for runs 7, 8, and 9 ranged from less than 15 to 37 ppm. The concentration of methane was below the 10-ppm detection limit. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

The decomposition of AN by WAO is enhanced when a reducing agent such as acetic acid is present; however, acetic acid is not as effective as was phenol. The data also suggest that reaction 1 describes the overall oxidation reaction during these tests.

Table 9. Wet air oxidation results—AN, 5 g/L + biosludge.

Analyses	Feed	AN 260 °C	AN 280 °C	AN 300 °C
Run Number	—	10	11	12
An. Number	51087	51088	51089	51090
COD, mg/L	810	243	143	210
COD Destruction %	—	70.0	82.4	74.0
Nonpurgable Organic Carbon, mg/L	38.2	100	41	30
BOD	<30	57	<10	<10
BOD/COD	—	0.23	—	—
Sol Chloride, mg/L	160	133	133	130
pH	1.25	1.28	1.28	1.27
Nitrate- N, mg/L	948	347	98	2.9
Total Kjeldahl Nitrogen, mg/L	1147	472	191	71
Ammonia-N, mg/L	912	501	195	66
Nitrite, mg/L	<0.5	<0.5	5	<0.5
N ₂ in OS-Gas-N, mg/L	—	734	1091	1154
N ₂ O in OS-Gas-N, mg/L	—	0	63	84
% Nitrogen in Offgas	—	35	55.1	59.1
% Nitrogen Removed From Liquid	—	60.9	85.9	93.4
Suspended Solids, mg/L	648	<5	<5	<5
Suspended Ash, mg/L	64	<5	<5	<5
Total Solids, mg/L	8110	7980	8268	8512
Total Ash, mg/L	570	600	672	752

Solution with 5 g/L AN + biosludge. Table 9 contains the analytical results from the WAO testing of the AN + biosludge solution. The autoclave feed was analyzed and had a total nitrogen concentration of 2,095 mg/L, a suspended solids concentration of 648 mg/L, and a measured COD concentration of 810 mg/L. The AN + biosludge solution was oxidized in a helium atmosphere at three different temperatures.

The AN significantly decomposed at 260 °C (run 10): 61 percent, according to the analyses of the liquid, but only 35 percent according to the offgas. No measurable quantity of nitrous oxide was detected in the offgas from run 10; however, as the oxidation temperature increased (runs 11 and 12) a small concentration of nitrous oxide was detected. The destruction of COD was calculated at 70 percent for run 10.

Increasing the oxidation temperature to 280 and 300 °C improved the decomposition of AN to 86 and 93 percent, respectively, based on the loss of total nitrogen from the oxidized effluent. The imbalance between the AN decomposition in the liquid and the amount produced in the gas phase was still present. Higher levels of COD and NPOC destruction were obtained by increasing the oxidation temperature. The suspended solids were successfully destroyed at all of the oxidation temperatures. The suspended solids in the oxidized effluents were less than 5 mg/L. Nitrate-N and ammonia-N decreased as the oxidation temperature increased. A direct comparison of AN decomposition to reaction 1 can not be made because of the unknown forms of nitrogen in the biosludge. The data do indicate that reaction 1 was predominant and that, at 300 °C, the AN decomposition was nitrate-N limited.

The concentrations of THC for runs 10, 11, and 12 ranged between 50 and 87 ppm. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B. The concentration of methane was below the 10-ppm detection limit.

The decomposition of AN by WAO is enhanced when a reducing agent such as biosludge is present. Biosludge and phenol have nearly the same effect on the decomposition of AN.

KDN Testing

Solution with 10 g/L KDN. Table 10 provides the analytical results from the WAO testing of the KDN solution. The autoclave feed was not analyzed so the calculated values were used to determine the percent destruction and formation of nitrogen compounds. The autoclave feed solution had a calculated total nitrogen concentration of 2,896 mg/L. The KDN solution was oxidized in a helium atmosphere at three different temperatures.

KDN will decompose to nitrate-N and nitrous oxide; approximately 45 percent of the calculated nitrogen added to the autoclave feed ends up as nitrous oxide and 35 percent is converted to nitrate-N. The products of the decomposition of the KDN indicate that reaction 2 is not representative of the overall reaction. Small concentrations of nitrogen gas and nitrite-N were detected. The amount of KDN that decomposed and the products of the decomposition appear to be independent of the oxidation temperature. An imbalance between nitrogen lost in the liquid to that produced in the gas phase still exists, thus pointing out an error in the measuring of one or more of the nitrogen products.

Table 10. Wet air oxidation results—KDN, 10 g/L.

Analyses	Feed, Calculated Concentration	KDN 260 °C	KDN 280 °C	KDN 300 °C	KDN 280 °C With Copper
Run Number	—	13	14	15	15a
An. Number	—	50449	50450	50451	50448
pH	1.11	1.58	1.57	1.59	1.6
Sol. Chloride, mg/L	—	<5	<5	<5	<5
Nitrate- N, mg/L	—	947	998	949	802
Total Kjeldahl Nitrogen, mg/L	2896*	<2	<2	<2	<2
Ammonia-N, mg/L	—	<2	<2	<2	<2
Nitrite, mg/L	—	9.6	9.2	14.4	9.6
N ₂ in Offgas-N, mg/L	—	210	147	21	21
N ₂ O in Offgas-N, mg/L	—	1279	1175	1175	1238
% Nitrogen in Offgas	—	51.4	45.6	41.3	43.5
% Nitrogen Removed From Liquid	—	66.9	65.2	66.7	72.0
Suspended Solids, mg/L	—	<5	<5	<5	<5
Suspended Ash, mg/L	—	<5	<5	<5	<5
Total Solids, mg/L	—	6916	9564	9476	8152
Total Ash, mg/L	—	5684	7992	8096	6644

*Total calculated nitrogen

An additional oxidation was done with a copper catalyst. The catalyst had no significant effect on the products obtained by the WAO.

Solution with 10 g/L KDN + 500 mg/L phenol. Table 11 gives the analytical results from the WAO testing of the KDN + phenol solution. The autoclave feed solution had a calculated total nitrogen concentration of 2,896 mg/L and a calculated COD concentration of 1,191 mg/L. The KDN + phenol solution was oxidized in a helium atmosphere at three different temperatures.

Table 11. Wet air oxidation results—KDN, 10 g/L + phenol, 500 mg/L.

Analyses	Feed, Calculated Concentration	KDN 260 °C	KDN 280 °C	KDN 300 °C
Run Number	—	16	17	18
An. Number	—	50445	50446	50447
COD, mg/L	1191	<85	<85	<85
COD Destruction %	—	>93	>93	>93
Nonpurgable Organic Carbon, mg/L	383	9.5	10.1	8.4
BOD	—	<10	<10	<10
Sol Chloride, mg/L	—	12	11	<5
pH	1.11	1.85	1.87	1.88
Nitrate- N, mg/L	—	498	486	509
Total Kjeldahl Nitrogen, mg/L	2896*	4.4	<2	<2
Ammonia-N, mg/L	—	4	<2	<2
Nitrite, mg/L	—	1	1	2
N ₂ in Offgas-N, mg/L	—	288	316	349
N ₂ O in Offgas-N, mg/L	—	1605	1329	1471
% Nitrogen in Offgas	—	65.4	56.8	62.8
% Nitrogen Removed From Liquid	—	82.6	83.2	82.3
Suspended Solids, mg/L	—	<5	<5	<5
Suspended Ash, mg/L	—	<5	<5	<5
Total Solids, mg/L	—	6568	6824	6956
Total Ash, mg/L	—	4996	5760	5740

*Total calculated nitrogen

The destruction of phenol and the decomposition of KDN were independent of the testing temperatures. A comparison of the 260, 280, and 300 °C test conditions (runs 16, 17, and 18) showed no significant differences in the oxidation products. The analyses of the liquid indicate that 82 percent of the KDN nitrogen was removed, but only approximately 60 percent of the total nitrogen in the autoclave feed was found in the gas phase.

Using the KDN as the oxidizing agent gave excellent destruction of the phenol compound. The oxidation of COD and NPOC was greater than 93 and 97 percent, respectively. Phenol affected the form of nitrogen produced. The organic compound appears to lower the concentration of nitrate that forms and enhances the production of nitrous oxide and nitrogen gas. This was determined by comparing Table 10 with Table 11.

The majority of the nitrogen in the offgas was in the form of nitrous oxide. The concentrations of THC for runs 16, 17, and 18 ranged between 15 and 16 ppm. The concentration of methane was below the 10-ppm detection limit. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

Solution with 10 g/L KDN + 1,000 mg/L acetic acid. Table 12 contains the analytical results from the WAO testing of the KDN + acetic acid solution. The autoclave feed solution had a calculated total nitrogen concentration of 2,896 mg/L and a calculated COD concentration of 1,091 mg/L. The KDN + acetic acid solution was oxidized in a helium atmosphere at three different temperatures.

The destruction of acetic acid and the decomposition products from KDN depended on the testing temperatures. The data show a general trend of decreasing nitrate-N concentration and increasing COD destruction as the oxidation temperature was increased. The COD destruction ranged from 64 to 92 percent for the 260, 280, and 300 °C tests (runs 19, 20, and 21). The analyses of the liquid indicate that 75 to 81 percent of the KDN nitrogen was removed from the liquid but only approximately 60 percent of the total nitrogen in the autoclave feed was found in the gas phase.

A high level of destruction of the acetic acid compound was obtained when KDN was the oxidizing source. Acetic acid is typically a by-product of the oxidation process and is difficult to oxidize in the standard WAO environment at temperatures below 300 °C. The data indicate that the oxidizing species liberated from the KDN decomposition is a stronger oxidizer than that found in a standard WAO system. As with the phenol, the acetic acid compound appears to lower the concentration of nitrate-N that forms and enhances the production of nitrous oxide and nitrogen gas. This was determined by comparing data from Tables 10 and 12.

Table 12. Wet air oxidation results—KDN, 10 g/L + acetic acid, 1 g/L.

Analyses	Feed, Calculated Concentration	KDN 260 °C	KDN 280 °C	KDN 300 °C
Run Number	—	19	20	21
An. Number	—	50439	50440	50441
COD, mg/L	1091	388	187	85
COD Destruction %	—	64	83	92
Nonpurgable Organic Carbon, mg/L	409	139	92	34
BOD	—	155	61	<10
BOD/COD	—	0.40	0.32	—
pH	1.11	1.75	1.62	1.64
Nitrate- N, mg/L	—	710	563	537
Total Kjeldahl Nitrogen, mg/L	2896*	<2	<2	<2
Ammonia-N, mg/L	—	<2	<2	<2
Nitrite, mg/L	—	6	5	
N ₂ in Offgas-N, mg/L	—	294	84	111
N ₂ O in Offgas-N, mg/L	—	1405	1133	1640
% Nitrogen in Offgas	—	58.6	42.0	60.4
% Nitrogen Removed From Liquid	—	75.3	80.3	81.2
Suspended Solids, mg/L	—	<5	<5	<5
Suspended Ash, mg/L	—	<5	<5	<5
Total Solids, mg/L	—	7288	7200	7496
Total Ash, mg/L	—	5764	4944	5500

*Total calculated nitrogen

The offgas analyses indicated that the majority of the nitrogen was in the form of nitrous oxide. The concentrations of THC for runs 19, 20, and 21 ranged between 15 and 16 ppm. The concentration of methane was below the 10-ppm detection limit. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

Solution with 10 g/L KDN + biosludge. Table 13 gives the analytical results from the WAO testing of the KDN + biosludge mixture. The autoclave feed was analyzed and had a total nitrogen concentration of 956 mg/L, a suspended solids concentration

of 640 mg/L, and a measured COD concentration of 832 mg/L. The data indicate that the nitrogen in the KDN component does not respond to the analytical methods. The total nitrogen calculated in the feed would be approximately 2,896 mg/L. Because of the error expected in the measured total nitrogen value, the calculated theoretical total nitrogen value was used to determine percent nitrogen removal. The KDN + biosludge mixture was oxidized in a helium atmosphere at three different temperatures.

Oxidation temperature had a slight effect on the COD destruction, NPOC destruction, and the percent nitrogen removed from the liquid. All three of these values

Table 13. Wet air oxidation results—KDN, 10 g/L + biosludge.

Analyses	Feed, Calculated Concentration	KDN 260 °C	KDN 280 °C	KDN 300 °C
Run Number	—	22	23	24
An. Number	51091	51094	51092	51093
COD, mg/L	832	118	84	<84
COD Destruction %	—	85.8	89.9	>90
Nonpurgable Organic Carbon, mg/L	33	33	23	6.7
BOD	<30	<10	<10	<10
Sol. Chloride, mg/L	139	133	125	130
pH	1.23	1.35	1.35	1.43
Nitrate- N, mg/L	892	594	570	482
Total Kjeldahl Nitrogen, mg/L	64	7.1	2.2	<2
Ammonia-N, mg/L	25	4	<2	<2
Nitrite, mg/L	<0.5	4.2	4.9	26
N ₂ in Offgas-N, mg/L	—	231	252	261
N ₂ O in Offgas-N, mg/L	—	1384	1342	1350
% Nitrogen in Offgas*	—	55.8	55.0	55.6
% Nitrogen Removed From Liquid	—	79.2	80.1	82.4
Suspended Solids, mg/L	640	<5	<5	<5
Suspended Ash, mg/L	<50	<5	<5	<5
Total Solids, mg/L	11420	9028	10804	9172
Total Ash, mg/L	6350	6932	8520	6780

*Based on theoretical nitrogen feed concentrations

showed a small increase as the oxidation temperature was increased. The nitrate-N concentration in the oxidized effluent declined slightly as the oxidation temperature was increased. Approximately 80 percent of the nitrogen from the KDN was removed during the oxidation process, according to the analyses of the liquid.

KDN appears to be an excellent oxidizer, the COD destruction ranging from 85 to greater than 90 percent. The suspended solids were successfully destroyed at all of the oxidation temperatures. The suspended solids in the oxidized effluents were less than 5 mg/L.

The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B. The concentrations of THC for runs 22, 23, and 24 ranged between 31 and 58 ppm. The concentration of methane was below the 10-ppm detection limit.

AN + KDN Solutions—Simulated PSAN

Solution with 5 g/L AN + 10 g/L KDN. There is currently no production waste from AN-based rocket motors, so the actual composition of the wastewater, and the ratio of AN to KDN, is unknown. Therefore, this is simulated PSAN wastewater. Table 14 contains the analytical results from the WAO testing of the AN + KDN solution. The autoclave feed was not analyzed, so the theoretical values were used to determine the percent destruction and formations of nitrogen compounds. The autoclave feed solution had a calculated total nitrogen concentration of 4,646 mg/L. The AN + KDN solution was oxidized in a helium atmosphere at three different temperatures.

The presence of AN did not inhibit the decomposition of the nitrogen in the KDN compound. The removal of nitrogen from the liquid phase ranged from 53 to 66 percent. The majority of the nitrogen removed ended up as nitrous oxide. At 300 °C the AN was more efficiently decomposed than it was by itself (data from Table 5), meaning that KDN may enhance AN decomposition. However, there still was approximately 400 mg/L of ammonia-N remaining for decomposition with excess nitrate-N. It is anticipated that a higher oxidation temperature may have increased the amount of AN decomposition.

The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B. The concentrations of THC for runs 25, 26, and 27 ranged between 15 and 19 ppm. The concentration of methane was below the 10-ppm detection limit. No oxygen was detected in the offgas.

Solution with 5 g/L AN + 10 g/L KDN + 1,000 mg/L phenol. Table 15 gives the analytical results from the WAO testing of the AN + KDN + phenol solution. The

Table 14. Wet air oxidation results—AN 5 g/L + KDN, 10 g/L.

Analyses	Feed, Calculated Concentration	260 °C	280 °C	300 °C
Run Number	—	25	26	27
An. Number	—	50442	50443	50444
pH	1.11	1.33	1.26	1.27
Nitrate- N, mg/L	875	1504	1428	1220
Total Kjeldahl Nitrogen, mg/L	3771	655	609	361
Ammonia-N, mg/L	875	772	670	399
Nitrite, mg/L	—	<0.5	<0.5	<0.5
N ₂ in Offgas-N, mg/L	—	378	327	522
N ₂ O in Offgas-N, mg/L	—	1259	1437	1546
% Nitrogen in Offgas*	—	35.2	37.9	44.5
% Nitrogen Removed From Liquid	—	53.5	56.2	65.9
Suspended Solids, mg/L	—	<5	<5	<5
Suspended Ash, mg/L	—	<5	<5	<5
Total Solids, mg/L	—	10884	11252	9392
Total Ash, mg/L	—	5728	5996	5832

*Based on theoretical nitrogen feed concentrations

autoclave feed solution had a calculated total nitrogen concentration of 4,646 mg/L and a calculated COD concentration of 2,382 mg/L. The AN + KDN + phenol solution was oxidized in a helium atmosphere at three different temperatures.

The destruction of the phenol and the decomposition of KDN and AN were for the most part independent of the testing temperatures. A comparison of the 260, 280, and 300 °C test conditions (runs 28, 29, and 30) showed no significant differences in the oxidation products. AN decomposition may have slightly increased at 300 °C. The analyses of the liquid indicate that approximately 80 percent of the nitrogen was removed from the liquid.

Excellent destruction of the phenol compound was obtained when using the KDN and AN as the oxidizing sources. The oxidation of COD and NPOC was greater than 96 and 97 percent, respectively. The presence of phenol improved the AN decomposition, as determined in previous testing. A higher level of AN decomposition may be

Table 15. Wet air oxidation results—AN 5 g/L + KDN, 10 g/L + phenol, 1000 mg/L.

Analyses	Feed, Calculated Concentration	260 °C	280 °C	300 °C
Run Number	—	28	29	30
An. Number	—	50499	50500	50501
COD, mg/L	2382	<85	<85	<85
COD Destruction %	—	>96	>96	>96
Nonpurgable Organic Carbon, mg/L	766	24	6.8	2.3
BOD	—	<10	<10	<10
Sol. Chloride, mg/L	—	<5	5.5	5.5
pH	1.2	1.69	1.68	1.69
Nitrate- N, mg/L	875	661	636	537
Total Kjeldahl Nitrogen, mg/L	3771	336	303	210
Ammonia-N, mg/L	875	330	326	277
Nitrite, mg/L	—	<0.5	<0.5	<0.5
N ₂ in Offgas-N, mg/L	—	1240	1696	1401
N ₂ O in Offgas-N, mg/L	—	1515	1596	1425
% Nitrogen in Offgas*	—	59.2	70.8	60.8
% Nitrogen Removed From Liquid	—	78.5	79.7	83.9
Suspended Solids, mg/L	—	<5	<5	<5
Suspended Ash, mg/L	—	<5	<5	<5
Total Solids, mg/L	—	9000	8972	9008
Total Ash, mg/L	—	6124	7644	6248

*Based on theoretical nitrogen feed concentrations

possible if the phenol concentration was increased. The data indicate that the oxidations may have been limited by the concentration of reducing agent.

The offgas analyses indicated that both nitrogen gas and nitrous oxide were present. The concentrations of THC for runs 28, 29, and 30 were below the 15-ppm detection limit. The concentration of methane was below the 10-ppm detection limit. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

Solution with 5 g/L AN + 10 g/L KDN + 2,000 mg/L acetic acid. Table 16 provides the analytical results from the WAO testing of the AN + KDN + acetic acid solution. The autoclave feed solution had a calculated total nitrogen concentration of 4,646 mg/L and a calculated COD concentration of 2,182 mg/L. The AN + KDN + acetic acid solution was oxidized in a helium atmosphere at three different temperatures.

The results showed that 78 to 86 percent of the nitrogen was removed from the liquid. The amount removed depended on the oxidation temperature. The concentrations of ammonia-N and nitrate-N in the effluent decreased as the oxidation temperature was increased. The decomposition reactions of the KDN and AN appear to

Table 16. Wet air oxidation results—AN 5 g/L + KDN, 10 g/L + acetic acid, 2 g/L.

Analyses	Feed, Calculated Concentration	260 °C	280 °C	300 °C
Run Number	—	31	32	33
An. Number	—	50502	50503	50504
COD, mg/L	2182	596	553	208
COD Destruction %	—	73	75	90
Nonpurgable Organic Carbon, mg/L	409	251	233	108
BOD	—	292	278	72
BOD/COD	—	48.9	50.2	34.6
Sol. Chloride, mg/L	—	5.5	<5	<5
pH	1.11	1.54	1.53	1.57
Nitrate- N, mg/L	875	872	821	609
Total Kjeldahl Nitrogen, mg/L	3771	145	91	2.3
Ammonia-N, mg/L	875	192	97	<2
Nitrite, mg/L	<0.5	<0.5	<0.5	9.2
N ₂ in Offgas-N, mg/L	—	1489	1400	1696
N ₂ O in OS-Gas-N, mvL	—	1173	1286	1471
% Nitrogen in Offgas*	—	57.3	57.8	68.2
% Nitrogen Removed From Liquid	—	78.1	80.4	86.6
Suspended Solids, mg/L	—	<5	<5	<5
Suspended Ash, mg/L	—	<5	<5	<5
Total Solids, mg/L	—	8364	8124	8240
Total Ash, mg/L	—	6372	6108	6592

*Based on theoretical nitrogen feed concentrations

be different when the reducing agent was changed from phenol to acetic acid. The AN decomposition reaction was ammonia-N limited, which was not the case when phenol was used. Higher levels of nitrogen removal and COD destruction may be possible if additional ammonia-N was added at 300 °C.

Destroying the acetic acid compound appears to be more difficult than destroying phenol. The destruction of COD ranged from 73 to 90 percent as the oxidation temperature was increased. The level of acetic acid destruction is significantly higher than would be expected by a standard WAO using air as the oxygen source.

The offgas analyses showed that both nitrogen gas and nitrous oxide were present. The concentrations of THC for runs 31, 32, and 33 ranged between 16 and 33 ppm. The concentration of methane was below the 10-ppm detection limit. The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

Solution with 5 g/L AN + 10 g/L KDN + biosludge. Table 17 gives the analytical results from the WAO testing of the AN + KDN + biosludge mixture. The autoclave feed was analyzed and found to have a total nitrogen concentration of 923 mg/L, a suspended solids concentration of 1,240 mg/L, and a measured COD concentration of 932 mg/L. The data indicate that the nitrogen in the KDN compound does not respond to the analytical methods. The total nitrogen calculated in the feed would be approximately 4,646 mg/L. Because of the error expected in the measured total nitrogen value, the calculated theoretical total nitrogen value was used to determine percent nitrogen removal. The AN + KDN + biosludge mixture was oxidized in a helium atmosphere at three different temperatures.

Oxidation temperature had a slight effect on the NPOC destruction and the percent nitrogen removed from the liquid. The nitrate-N concentration in the oxidized effluent declined slightly as the oxidation temperature was increased. The analyses of the liquid indicate that approximately 80 percent of the nitrogen from the liquid was removed during the oxidation process. The AN decomposition reaction was ammonia-N limited. The ammonia concentration in the 300 °C oxidized effluent was less than 4 mg/L.

AN + KDN appear to be excellent oxidizers. The COD destruction was greater than 91 percent. The suspended solids were successfully destroyed at all of the oxidation temperatures. The suspended solids in the oxidized effluents were less than 5 mg/L.

The concentrations of THC in the offgas for runs 34, 35, and 36 ranged between 18 and 22 ppm. The concentration of methane was below the 10-ppm detection limit.

Table 17. Wet air oxidation results—AN 5 g/L + KDN, 10 g/L + biosludge.

Analyses	Concentration	260 °C	280 °C	300 °C
Run Number	—	34	35	36
An. Number	51095	51096	51097	51098
COD, mg/L	932	<84	<84	<84
COD Destruction %	—	>91	>91	>91
Nonpurgable Organic Carbon, mg/L	40	11	6.8	2.6
BOD	<30	<30	<30	<30
Sol. Chloride, mg/L	136	109	126	132
pH	1.22	1.27	1.27	1.28
Nitrate- N, mg/L	1942	823	792	692
Total Kjeldahl Nitrogen, g/L	923	191	27	12
Ammonia-N, mg/L	938	201	24	3.5
Nitrite, mg/L	0.7	<0.5	<0.5	4.4
N ₂ in Offgas-N, mg/L	—	1308	1538	1425
N ₂ O in Offgas-N, mg/L	—	1286	1331	1448
% Nitrogen in Offgas*	—	55.8	68.2	61.8
% Nitrogen Removed From Liquid*	—	78.2	82.3	84.7
Suspended Solids, mg/L	1240	<5	62	<5
Suspended Ash, mg/L	330	<5	62	<5
Total Solids, mg/L	15490	12628	9104	9136
Total Ash, mg/L	6370	8812	6488	6796

*Based on theoretical nitrogen feed concentrations.
The material tests were performed using the "as welded" stressed coupons.

The offgas analyses and the autoclave charge conditions for each run are listed in Appendix B.

Results of Testing Potential WAO System Construction Materials

The objective of this screening test was to identify types of alloys that could be considered candidate materials for construction of a full-scale WAO system. Three tests

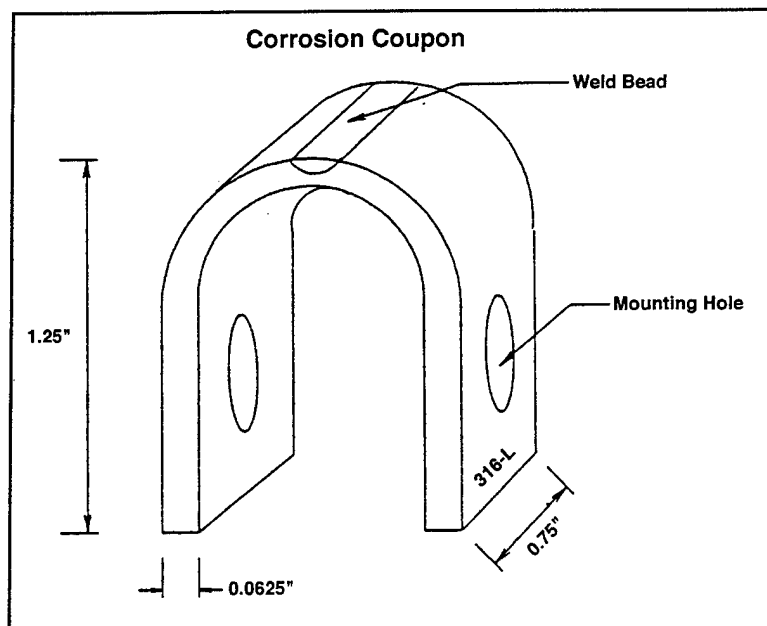


Figure 2. Material test coupon.

were conducted at 300 °C for 120 hours using AN + phenol, KDN + phenol, and AN + KDN + phenol solutions.

The alloys selected for the screening are listed in Table 18, along with their nominal chemical compositions. These materials were selected for their known corrosion resistance in the WAO environment. The metal coupons consist of a 0.75-in. wide U-bend strip made from a 16-gauge annealed sheet. The coupons have a 0.75-in. weld along the bottom of the curved surface (Figure 2). The material tests were performed using the "as welded" stressed coupons.

Table 18. Composition of evaluated materials.

Alloy	Fe	Cr	Ni	C	Cu	Mo
Nominal Chemical Composition, %						
316-L Stainless Steel	bal	18	13	0.03	—	2.25
Alloy 20CB-3	bal	20	34	0.07	3.5	2.50
Hastelloy C-276	5	16	bal	0.02	—	16
Inconel 625	5	21	bal	0.05	—	9
Titanium Grade 2	Commercially pure Titanium					

Table 19. Materials of construction testing results.

Alloy Tested	General Corrosion Rates, MPY	Comments
316-L Stainless Steel	130	Stress Corrosion Cracking
Alloy 20CB-3	11	Stress Corrosion Cracking
Hastelloy C-276	11	Stress Corrosion Cracking
Inconel 625	5.8	Stress Corrosion Cracking
Titanium Grade 2	Weight Gain	No Localized Corrosion

MPY: Mills per year (1/1000th of an inch per year).

AN + Phenol

The results from testing the materials of construction in the AN + phenol solution are presented in Table 19. The stainless steel (316-L and Alloy 20) and nickel base alloys (C-276 and 625) would not be acceptable for constructing a WAO system. These materials had general corrosion rates of greater than 5 mpy (1 mpy = 0.001 in./year), and microscopic analyses found signs of stress corrosion cracking, which was intergranular.

A strong odor and a small amount of suspended material was observed when researchers were discharging the autoclave after testing the 316-L material. They associated the odor with a typical oxygen-deficient WAO condition. This was not observed with the other materials, and is expected to have caused 316-L's high corrosion rate.

As the corrosion results demonstrate, titanium grade 2 would be the best candidate, since it showed no signs of general or localized corrosion. However, testing the materials of construction over a longer term is recommended.

KDN + Phenol

Testing the materials of construction in the KDN + phenol solution (Table 20) indicates that the stainless steels (316-L and Alloy 20) and titanium grade 2 would be acceptable. The alloys had general corrosion rates of less than 2 mpy and there was no evidence of localized corrosion. The good performance of the stainless steel materials was somewhat unexpected because of the low pH and elevated temperature in the autoclave. Both 316-L and Alloy 20 would probably not perform acceptably if 100 mg/L of chloride was present in the test solutions.

The nickel base alloys (C-276 and 625) would not be acceptable, since they had general corrosion rates of greater than 5 mpy. Microscopic analyses found signs of intergranular stress corrosion cracking in the nickel base alloys.

AN + KDN + Phenol

The test results from the AN + phenol solution (Table 21) indicate that the stainless steels (316-L and Alloy 20) and titanium grade 2 would be acceptable. The alloys had general corrosion rates of less than 2 mpy and no evidence of localized corrosion was found. As in the last section, the good performance of the stainless steel materials was somewhat unexpected because of the low pH and elevated temperature; 316-L and Alloy 20 probably would not perform acceptably if chloride levels of over 100 mg/L were present in the test solutions.

The nickel base alloys (C-276 and 625) would not be acceptable as materials of construction. They had general corrosion rates of greater than 5 mpy, and microscopic analyses found signs of intergranular stress corrosion cracking.

Table 20. Materials of construction testing results.

Alloy Tested	General Corrosion Rates, MPY	Comments
316-L Stainless Steel	<2	No Localized Corrosion
Alloy 20CB-3	<2	No Localized Corrosion
Hastelloy C-276	39.9	Stress Corrosion Cracking
Inconel 625	15.9	Stress Corrosion Cracking
Titanium Grade 2	Weight Gain	No Localized Corrosion

MPY: Mills per year (1/1000th of an inch per year)

Table 21. Materials of construction testing results.

Alloy Tested	General Corrosion Rates, MPY	Comments
316-L Stainless Steel	<2	No Localized Corrosion
Alloy 20CB-3	<2	No Localized Corrosion
Hastelloy C-276	5.2	Stress Corrosion Cracking
Inconel 625	16.2	Stress Corrosion Cracking
Titanium Grade 2	Weight Gain	No Localized Corrosion

MPY: Mills per year (1/1000th of an inch per year).

4 Wet Air Oxidation of Hazardous Waste Sludge

WAO testing was also applied to a hazardous waste sludge generated at Radford Army Ammunition Plant (RAAP). These tests were conducted to determine if the use of AN as the oxidizer for sludges derived from energetics production would create any unexpected by-products not encountered in the control tests described above.

Sludge was obtained by RAAP personnel from the aerobic digester, which is part of their Biological Wastewater Treatment Plant. It was collected prior to belt filtration and was primarily liquid, with some noticeable solids. Workers composited 3 L of sludge as received and took a sample. The sludge was then spiked with approximately 30 mg/L of dinitrotoluene (DNT) dissolved in methanol. DNT was added because it could potentially accumulate in the sludge from treatment processes at the plant. The samples were stored at 4 °C. An analysis of the sludge is presented in Table 22.

All analyses were conducted in accordance with *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA, and WEF 1985) or *EPA Methods for Chemical Analysis of Water and Wastes* (EPA 1979), except for sludge volume index (SVI), which had to be modified owing to the small volumes of sludge available. Normally, 1 L of sludge is used for the SVI. In these analyses, 25 mL was used in a graduated cylinder.

Table 22. RAAP aerobic digester sludge characteristics.

	Composited Sludge	Spiked Composited Sludge
Chemical Oxygen Demand, mg/L	10500	14300
Total Suspended Solids, mg/L	8830	9310
Sludge Volume Index	100	44
Ammonia-N, mg/L	298	292
Nitrate-N, mg/L	0.035	0.044
Total Organic Carbon, mg/L	3340	3320
Biological Oxygen Demand, mg/L	3000	5200
Total Kjeldahl Nitrogen, mg/L	890	820

Although DNT was added to the samples, it was not detected in the sludge samples. No effort was made to completely arrest biological activity except for storage at 4 °C. There was evidently enough bioactivity present to degrade or transform the DNT. Another indication of bioactivity was that sufficient gas was generated to cause the sludge to rise. Rising sludge is common in aerobic wastewater treatment plants, where insufficient oxygen is available; the bacteria use nitrate in place of oxygen, releasing nitrogen gas. As a result, when the sludge volume index was measured on the spiked sludge, the sludge moved to the top of the graduated cylinder rather than the bottom.

The experiments with RAAP sludge were conducted in a 600-mL T-316 stainless steel reactor (Parr Instruments, Moline, IL). The reactor sits in a heating jacket that controls the temperature. It is equipped with a magnetically driven stirrer, cooling coils, pressure and temperature sensors, and sampling ports (Figure 3). The main difference between this reactor and that used at Zimpro-Passavant is that stirring rather than shaking keeps the contents mixed. The maximum temperature for this reactor was 350 °C and the maximum pressure was 3,000 psi. Experiments were carried out for 1 hour just as at Zimpro-Passavant for the AN and KDN studies.

The reactor temperature was regulated with a controller that activates the heating jacket until the desired temperature is reached. An internal cooling coil, hooked up to the municipal water supply, is used to cool the reactor down after the completion of the experiment. No oxygen or air charge was added to the reactor; the excess nitrate in the AN would be the source of the oxidant. The controller also set the speed

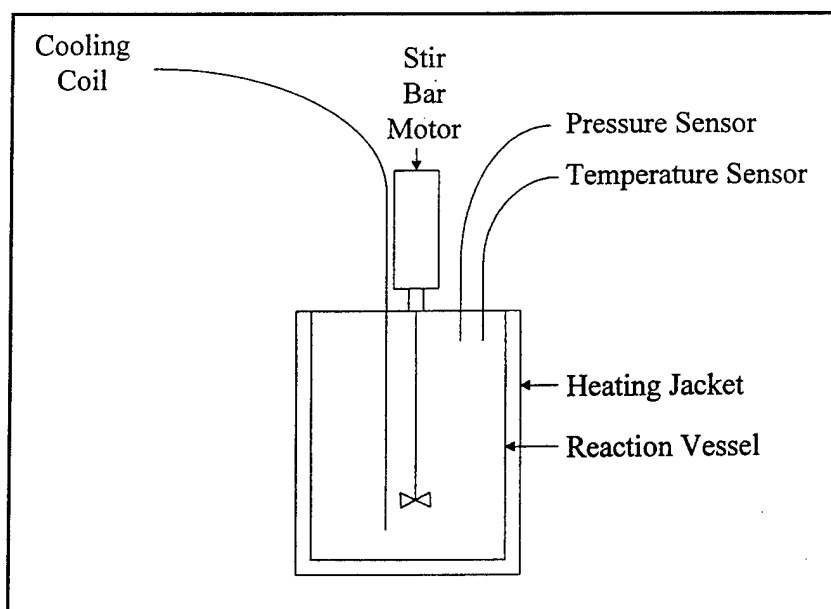


Figure 3. Wet Air Oxidation Reactor.

Table 23. Summary of RAAP sludge experimental conditions.

Temperature (°C)	Sludge (mL)	AN (mL)	mg COD available	mg Oxidant available
280	150	100	2100	2000
	170	80	2380	1600
	190	60	2660	1200
300	150	100	2100	2000
	170	80	2380	1600
	190	60	2660	1200
325	150	100	2100	2000
	170	80	2380	1600
	190	60	2660	1200

of the stirrer, and displayed the pressure inside the reactor. The reactor was operated at 280, 300 and 325 °C. When cooling commenced, the water lines would shake as the first water was introduced into the cooling coil and vaporized. Shaking ceased usually when the reactor got below 225 °C. The pressure in the reactor reached 900 psi at 280 °C, 1,220 psi at 300 °C and 1,800 psi at 325 °C.

The spiked, composited sludge was added to AN solutions to make up a total sample for WAO of 250 mL. The AN concentration was 100 g/L. Experiments were conducted with an excess of COD available for reaction with the AN, which has a theoretical oxygen excess of $\frac{1}{2}$ mole oxygen (16 g) per mole of AN (80), or 0.2 g oxygen/g AN. On the basis of the measured value of 14,300 mg/L COD in the spiked, composited sludge, the available COD is approximately 14 mg/mL. AN has 0.2 g of oxidant available per gram, thus the solution had 20 g/L available oxidant, or 20 mg/mL. Table 23 summarizes the conditions and available reactants (COD and oxidant) in the WAO experiments conducted with RAAP sludge.

SVI is an inverse measure of the density of the sludge. It was measured in these experiments because early observations showed that the large majority of the sludge solids were destroyed or converted into inorganic precipitates. The lower the SVI is, the denser the sludge is. Analytically, it is defined as the volume in milliliters occupied by 1 g of sludge solids. Reductions in the SVI indicate that the volume of sludge requiring disposal is also reduced. In addition to SVI, total suspended solids (TSS) and COD were measured for comparison to the data developed in the shaking autoclave experiments reported earlier.

Figures 4 through 6 show the reduction in COD, TSS, and SVI for the near stoichiometric tests in which 150 mL of sludge was mixed with 100 mL of AN solution. In these tests, there was 2,100 mg of COD mixed with 2,000 mg of available oxidant in the AN. Appendix C gives the final water quality data for the RAAP sludge.

Figure 4 shows that a high degree of COD reduction (>90%) was possible, but only at the highest temperature tested (325 °C). The suspended solids were dramatically reduced by all temperatures tested, meaning that the biomass was largely converted into soluble material (Figure 5). This is further supported by the SVI (Figure 6), which also indicates that the primary residues are soluble at all three temperatures tested, and that the volume of sludge remaining after treatment is relatively small.

Figures 7 through 9 show the results for a mixture of 170 mL sludge and 80 mL AN, which is a ratio of 2,380 mg COD to 1,600 mg oxidant. In this case, the reduction in COD declines to less than 80 percent (Figure 7). The highest reduction occurs only at the highest temperature tested (325 °C), just as in the previous three samples at near stoichiometric mixtures of COD and oxidant. However, the reduction in TSS and SVI (Figures 8 and 9) were very similar to the reductions at near-stoichiometric mixtures. This means that the sludge volume is reduced at less than stoichiometric mixtures.

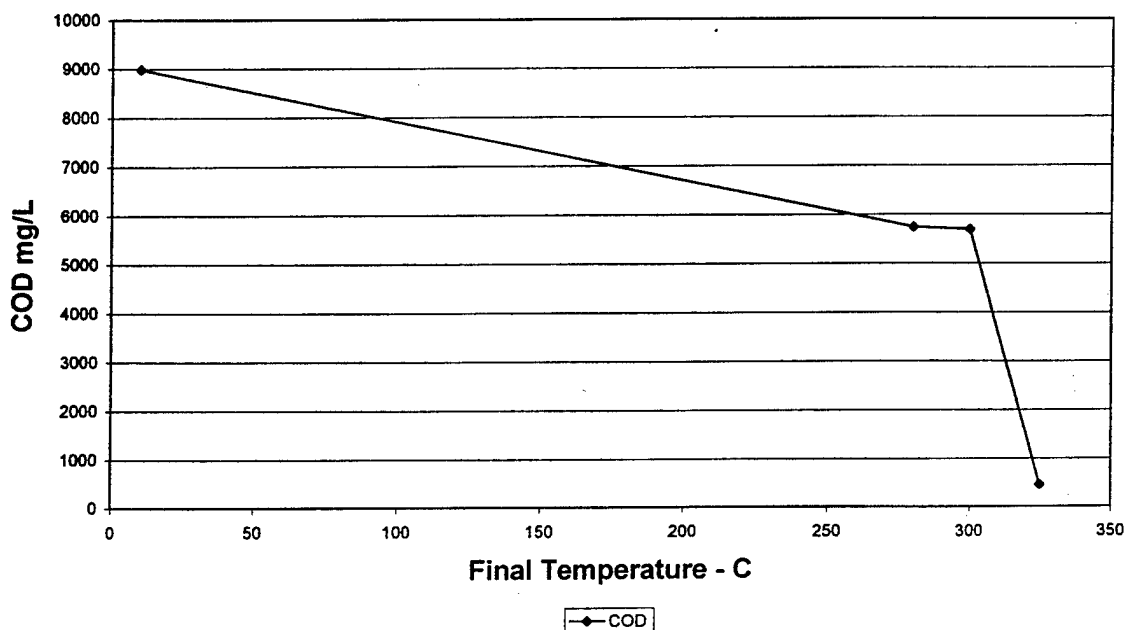


Figure 4. COD remaining vs. temperature — 150 mL sludge + 100 mL AN.

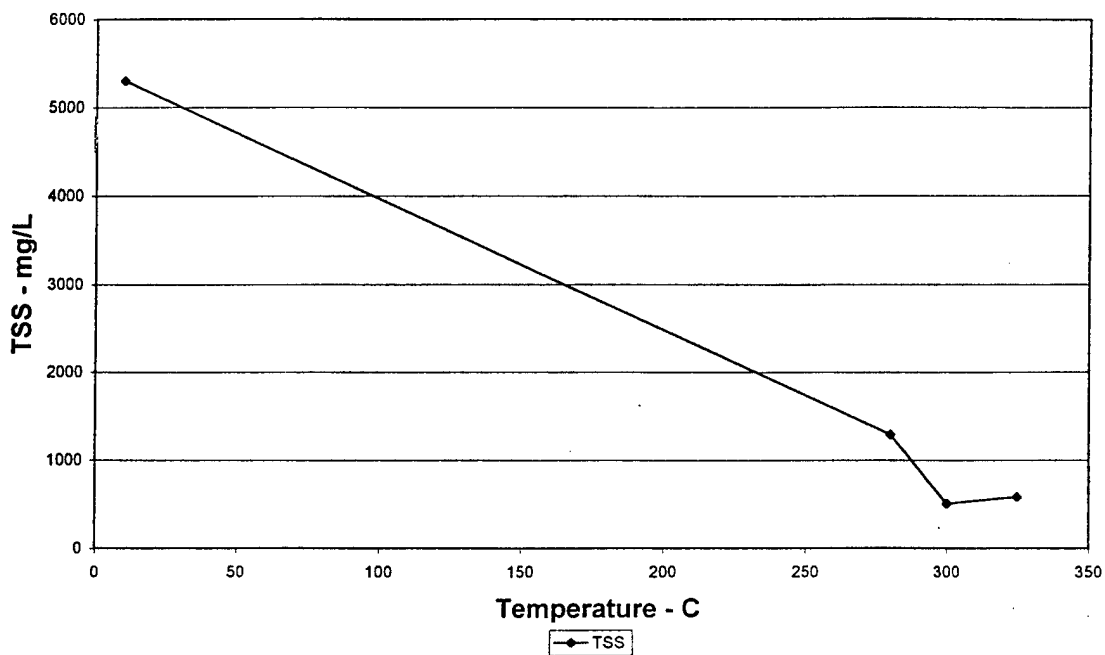


Figure 5. TSS remaining vs. temperature — 150 mL sludge + 100 mL AN.

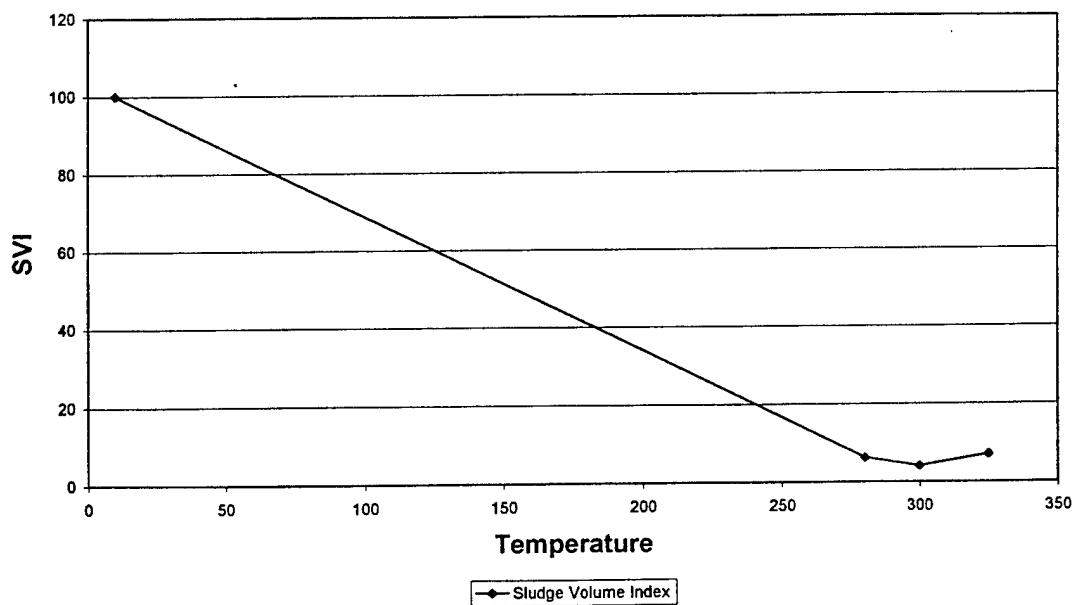


Figure 6. SVI vs. temperature — 150 mL sludge + 100 mL AN.

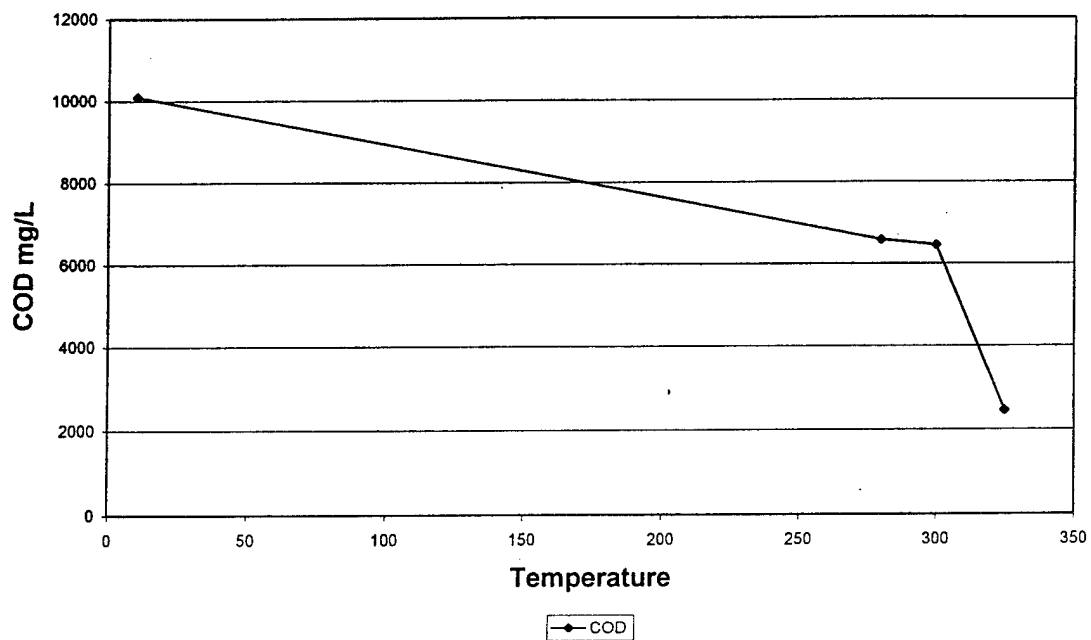


Figure 7. COD reduction vs. temperature — 170 mL sludge + 80 mL AN.

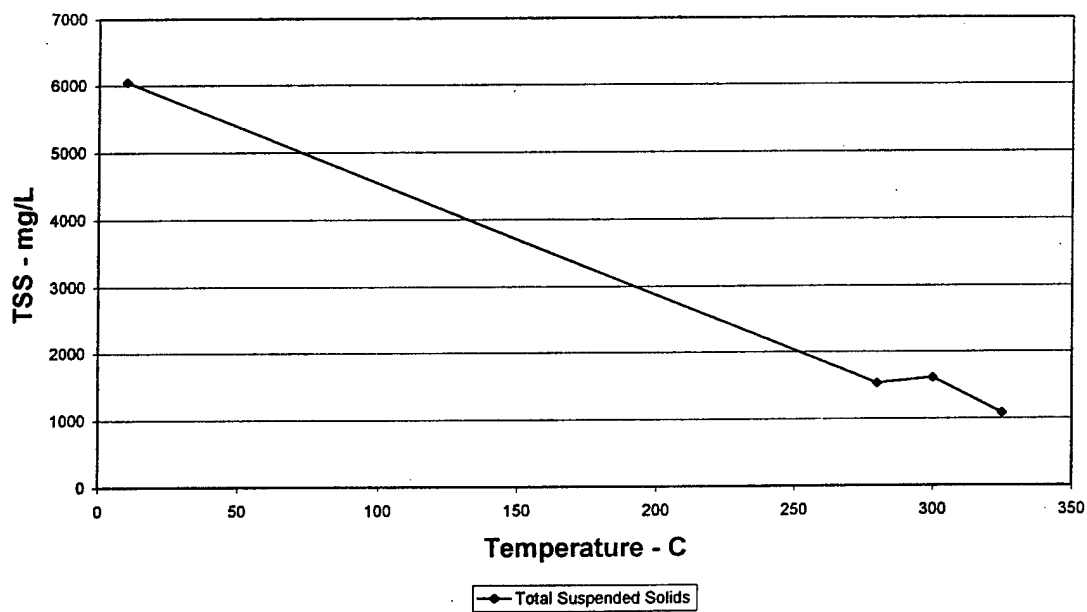


Figure 8. TSS reduction vs. temperature — 170 mL sludge + 80 mL AN.

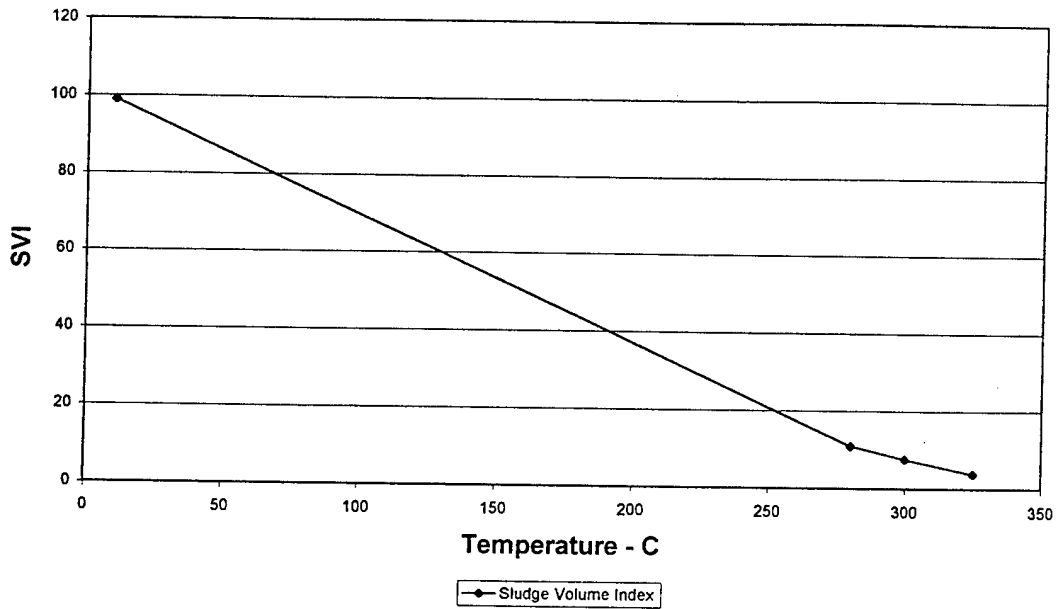


Figure 9. SVI vs. temperature — 170 mL sludge + 80 mL AN.

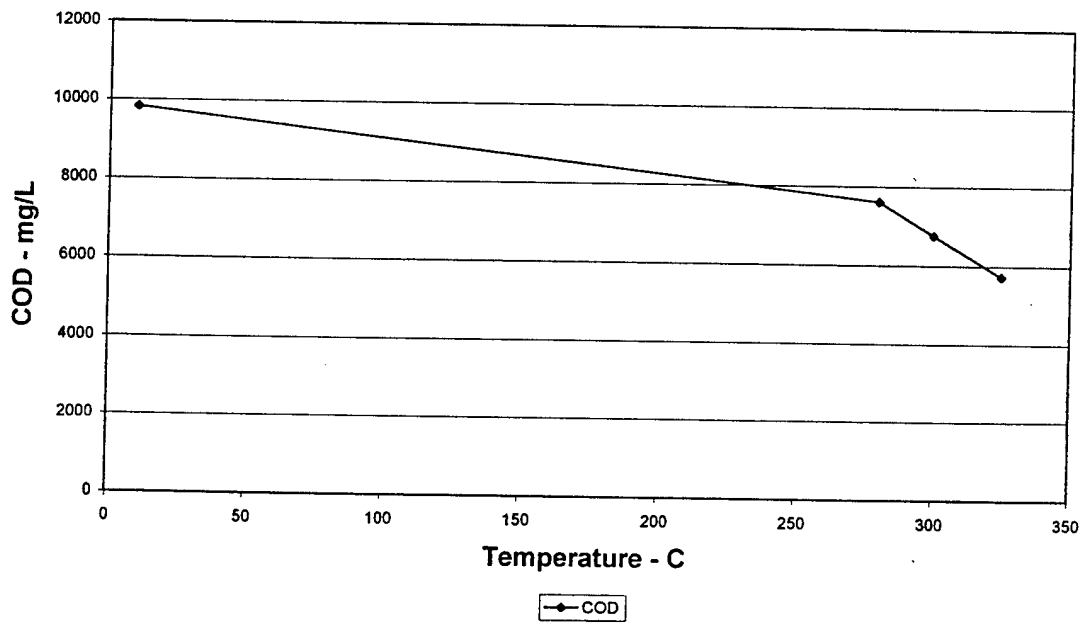


Figure 10. COD reduction vs. temperature — 190 mL sludge + 60 mL AN.

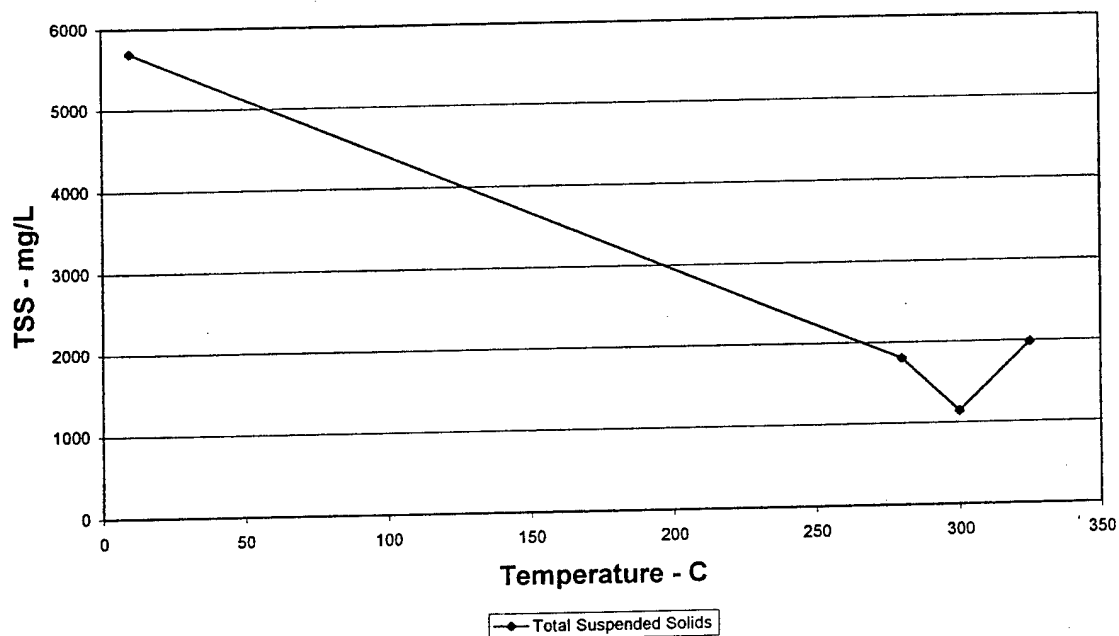


Figure 11. TSS reduction vs. temperature — 190 mL sludge + 60 mL AN.

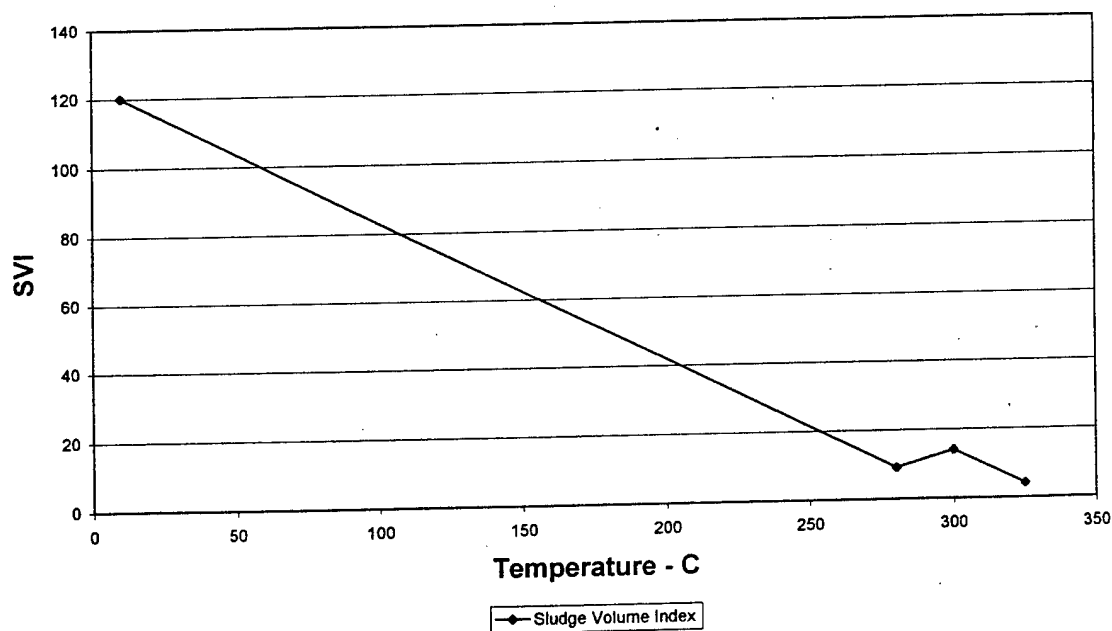


Figure 12. SVI vs. temperature — 190 mL sludge + 60 mL AN.

Similar results were obtained for a mixture of 190 mL sludge with 60 mL AN, which is a ratio of 2,660 mg COD to 1,200 mg AN, or more than 2:1. These results are shown in Figures 10 through 12. The reduction in COD declined again (Figure 10), but final TSS values, and final SVI values (Figures 11 and 12) remain low.

Comparing these results to those obtained in the shaking autoclave (Table 17) demonstrates that the RAAP sludge was somewhat more difficult to degrade. The COD was reduced by >95% in only one test at 325 °C, and much less at 300 and 280 °C. This is still well within the range of treatment temperatures used in WAO, but may require different materials to withstand the higher temperatures, or longer reaction times. However, another observation from the experiments conducted with RAAP sludge also favors the use of higher temperatures.

A translucent film of material was deposited on the cooling coils when the reaction temperature was 300 °C or less, but not at 325 °C. Samples of this material were collected and subjected to analysis by gas chromatography/mass spectrometry (GC/MS) and liquid chromatography. Unfortunately, there was insufficient concentration of any single material that could be identified by these analyses. This could lead to increases in the sludge remaining if a similar material were to form after cooling in a full scale system. This would need to be evaluated in any pilot scale test.

The overall results from the bench scale evaluation of treatment of a biological sludge in conjunction with disposal of waste AN say that there should be no undesirable by-products as long as the temperature is 325 °C or above. Refinements in the required temperature should be made in pilot testing of specific sludges before a system is designed. A side benefit of the co-disposal of sludge and waste AN by WAO is the dramatic reduction in the residual sludge. This is a major cost component of biological wastewater treatment plants, particularly for munitions plants, where the sludge has to be disposed of as a hazardous waste. WAO would be able to reduce the sludge to be disposed, and destroy the oxidant KDN.

5 Summary

Ammonium nitrate (AN) is a common substance that is mass produced at low cost. Reuse of waste AN would only be cost effective if the recycling costs were less than the market cost of commercial products. The market cost for AN is \$0.07–0.10/lb, compared to an estimated membrane separation cost of approximately \$0.60/lb. As a result, reuse of phase stabilized ammonium nitrate (PSAN) will not be cost effective if separation of the potassium dinitrimide (KDN) is required.

The AN can be effectively destroyed by wet air oxidation (WAO). This is a high pressure, high temperature treatment process, in which oxidants react with materials that would be stable under ambient conditions. Ammonia reacts with nitrate to form nitrogen gas. There is also excess oxidant that can be used to react with other complex organic wastes.

KDN is destroyed in the WAO process. However, a significant amount of nitrous oxide is present in the offgas. This may require additional air pollution control equipment if a facility has restricted nitrogen oxide emissions.

AN can be effectively used in treating a typical biological sludge from a munitions plant using WAO. This will simultaneously destroy the KDN and reduce the amount of sludge to be disposed of by approximately 90 percent, creating an attractive alternative where sludge is a hazardous waste. Savings from reduced sludge disposal will partially offset the cost of WAO and waste AN handling. In addition, it reduces the long term liability associated with sludge disposal in hazardous waste landfills.

References

- American Public Health Association, American Water Works Association, and Water Environment Federation (APHA, AWWA, and WEF), *Standard Methods for the Examination of Water and Wastewater* (1985).
- Bryan, L.A., and E.A. Bryan, *Programmable Controllers Theory and Implementation* (Industrial Text, 1988).
- Cole, J.P., and G.V.R. Holness, *Use Of Programmable Controllers for HVAC Control and Facilities Monitoring Systems*, ASHRAE Transactions Part 1 (ASHRAE, 1989), pp 492-497.
- Environmental Protection Agency (EPA), *EPA Methods for Chemical Analysis of Water and Wastes* (1979, Revised 1983).
- Hager, Robert, "The Next Step In PLC Support Software," *Control Engineering* (February 1991), pp 39-41.
- Ingrey, A., "Single Loop Controllers," *IEEE Computers and Instrumentation* (January 1988), pp 29-32.
- Means, *Environmental Cost Handling Options and Solutions (ECHOS) Handbook*, R.S. Means Company, Inc., Kingston, MA (1997).
- Modicon, *Modicon 984 Programmable Controller Systems Manual*, ch. 1 (Modicon, 1991), p 3.
- Pollard, Jeremy, "The Future of PLC Programming," *Control Engineering* (February 1995), pp 83-88.
- Schwenk David, "Single-Loop Digital Controllers In HVAC," *ASHRAE Transactions*, vol 94, pt 2 (1988), pp 1985-1994.
- Seibert, Iris, "Longevity of STD Bus Continues," *Control Engineering* (December 1991), pp 91-93.
- Technical Manual [TM] 5-815-3, Heating, Ventilating, and Air Conditioning (HVAC) Control Systems (Headquarters, Department of the Army [HQDA], Washington, DC, July 1991).

Appendix A: Cost Calculation for Reuse Alternatives

TABLE A-1
Separation of Ammonium Nitrate (AN) From Potassium Dinitrimide (KDN)
Using Reverse Osmosis
10 Gallons Per Minute Design Basis

Mobilization/Demobilization	ea	2	\$413.00	\$826.00	Means 022 200 274
Size Reduction/Pulverizer	ea	1	\$70,000.00	\$70,000.00	Dames & Moore
AN-Slurry Mix Tank	ea	1	\$32,000.00	\$32,000.00	Dames & Moore
Twin Reverse Osmosis (RO) System	ea	1	\$1,200,000.00	\$1,200,000.00	Purification Products
Reject Recovery Vessel	ea	1	\$100,000.00	\$100,000.00	Purification Products
Evaporator/Crystallizer	ea	1	\$900,000.00	\$900,000.00	Purification Products
High Pressure Pumps	ea	2	\$10,000.00	\$20,000.00	Purification Products

Subtotal

\$2,322,826.00

Health and Safety, Training and Equipment (2.5%)

Construction Contingencies (20%)

Total Initial Implementation Cost

Design, Engineering, and Construction Management (15%)

TOTAL CAPITAL COST

ANNUAL COST (10 years, 7%)

\$58,071.00

\$464,565.00

\$2,845,462.00

\$426,819.00

\$3,272,281.00

\$465,973.00

ANNUAL OPERATION AND MAINTENANCE COSTS

Operator Labor	hrs	625	\$40.00	\$25,000.00	Purification Products
Maintenance Labor	hrs	213	\$45.00	\$9,563.00	Purification Products
Electric Power	kw-hr	121,500	\$0.07	\$8,505.00	Purification Products
Water	gal	8,400,000	\$0.00025	\$2,100.00	Purification Products
Evaporator Steam	lb	112,433	\$1.35	\$151,784.00	D&M Estimate
Residue Disposal (reject and spent RO membranes)	ea	3,120	\$3.00	\$9,360.00	
D&M Estimate					

Annual O&M Total =

\$206,312.00

Total Annual Cost =

\$672,285.00

TABLE A-2

**Reuse of Pure Ammonium Nitrate (AN) as Fertilizer
10 Acre Site Basis
800 lbs AN per Acre**

Item	Unit	Quantity	Unit cost	Total cost	Reference
Mobilization/Demobilization	ea	2	\$413.00	\$826.00	Means 022 200 274
Size Reduction/Pelletization	ea	1	\$30,000.00	\$30,000.00	Dames & Moore
Push Rotary Fertilizer	acre	10	\$80.00	\$800.00	ECHOS 18 05 0409
Water Tank Truck, 3,000 gal (2 applications)	acre	20	\$40.00	\$800.00	ECHOS 14 05 0413
Shallow Soil Tilling	yd3	16,133	\$1.00	\$16,133.00	ECHOS 17 03 0257
Automated Sprinkler System	acre	10	\$4,000.00	\$40,000.00	ECHOS 18 05 0711
Subtotal				\$88,559.00	
Health and Safety, Training and Equipment (2.5%)				\$2,214.00	
Construction Contingencies (20%)				\$17,712.00	
Total Initial Implementation Cost				\$108,485.00	
Design, Engineering, and Construction Management (15%)				\$16,273.00	
TOTAL CAPITAL COST				\$124,757.00	
ANNUAL COST (10 years, 7%)				\$17,765.00	
ANNUAL OPERATION AND MAINTENANCE COSTS					
Water (20x per year @ 1,000 gal per acre)	gal	200,000	\$0.00025	\$50.00	D&M Estimate
General Maintenance Labor	mhour	520	\$45.00	\$24,300.00	D&M Estimate
Annual O&M Total =				\$24,350.00	
Total Annual Cost =				\$42,115.00	

TABLE A-3
Use of Ammonium Nitrate (AN) as an Oxidizer in Wet Air Oxidation
2 Gallons Per Minute Design Basis

Item	Unit	Quantity	Unit cost	Total cost	Reference
Mobilization/Demobilization	ea	2	\$413.00	\$826.00	Means 022 200 274
Size Reduction/Pulverizer	ea	1	\$30,000.00	\$30,000.00	Dames & Moore
AN-Slurry Mix Tank	ea	1	\$6,000.00	\$6,000.00	Dames & Moore
Stirred Tank Reactor	ea	1	\$756,000.00	\$756,000.00	Zimpro
Feed-Product Heat Exchanger	ea	1	\$72,000.00	\$72,000.00	Zimpro
High Pressure Pump	ea	1	\$36,000.00	\$36,000.00	Zimpro
Air Compressor	ea	1	\$84,000.00	\$84,000.00	Zimpro
Product Separator	ea	1	\$120,000.00	\$120,000.00	Zimpro
Air Pollution Control Device	ea	1	\$108,000.00	\$108,000.00	Zimpro
Subtotal				\$1,212,826.00	
Health and Safety, Training and Equipment (2.5%)				\$30,321.00	
Construction Contingencies (20%)				\$242,565.00	
Total Initial Implementation Cost				\$1,485,712.00	
Design, Engineering, and Construction Management (15%)				\$222,857.00	
TOTAL CAPITAL COST				\$1,708,569.00	
ANNUAL COST (10 years, 7 %)				\$243,300.00	
ANNUAL OPERATION AND MAINTENANCE COSTS					
Operator Labor	hrs	1,250	\$40.00	\$50,000.00	Zimpro
Maintenance Labor	hrs	425	\$45.00	\$19,125.00	Zimpro
Electric Power	kW-hr	243,000	\$0.07	\$17,010.00	Zimpro
Water	gal	16,800,000	\$0.00025	\$4,200.00	Zimpro
Residue Disposal (WAO and air poll. control device)	ea	ea	6,240	\$3.00	\$18,720.00
D&M Estimate					
Annual O&M Total =				\$109,055.00	
Total Annual Cost =				\$352,355.00	

Appendix B: Calculations for Shaking Autoclave Tests

Run # 1

Date: 9/18/95

Client: ARMY

Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	260 °C

Liquid Volume	250 ml
Head Space	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.1
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	240 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	<.2 %
CO	0.00 %
N ₂ O	0.00 %
THC	< 10 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.037 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	#N/A g/L
Nitrogen From N ₂ O	0.000 g/L

¹Volume measured

²Containing both organic and inorganic carbon

11:20 AM Last Modified 26-May-1993 9/19/95

Run # 2
Date: 9/15/95
Client: ARMY
Autodave Material: E>11

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
Volume ¹	0.00 /
CO ₂	0.00 %
O ₂	0.00 %
N ₂	0.90 %
CO	0.00 %
N ₂ O	0.10 %
THC	<15 ppm

Effluent

pH	1.1
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,660 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.189 g/L
Nitrogen From N ₂ O	0.021 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:24 AM Last Modified 26-May-1993 9/19/95

Run# 3
Date: 9/18/95
Client: ARMY
Autoclave Material: Ti-11

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	Head Space	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	240 psig
Volume ¹	0.00 /
CO ₂	0.00 %
O ₂	0.00 %
N ₂	0.50 %
CO	0.00 %
N ₂ O	0.40 %
THC	0 ppm

Effluent

pH	1.1
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume
Pressure @ Temperature 2,095 psig

Offgas Volume	4.037 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.101 g/L
Nitrogen From N ₂ O	0.081 g/L

¹Volume measured

²Containing both organic and inorganic carbon
8:39 AM Last Modified 26-May-1993 9/19/95

Run # 3a
Date: 9/18/95
Client: ARMY
Autodave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	Head Space	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	245 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	0.30 %
CO	0.00 %
N ₂ O	0.10 %
THC	< 15 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.116 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.062 g/L
Nitrogen From N ₂ O	0.021 g/L

¹Volume measured

²Containing both organic and inorganic carbon

11:59 AM Last Modified 26-May-1993 9/19/95

Run # 4
Date: 9/18/95
Client: ARMY
Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	Head Space	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
Volume ¹	0.00 /
CO ₂	1.80 %
O ₂	0.00 %
N ₂	4.60 %
CO	0.70 %
N ₂ O	0.00 %
THC	22 ppm

Effluent

pH	1.1
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.225 g/L
Nitrogen Produced	0.965 g/L
Nitrogen From N ₂ O	0.000 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:30 AM Last Modified 26-May-1993 9/19/95

Run #5

Date: 9/15/95

Client: ARMY

Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	260 psig
Volume1	0.00 /
CO ₂	2.50 %
O ₂	0.00 %
N ₂	5.00 %
CO	0.30 %
N ₂ O	0.00 %
THC	27 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,660 psig
Offgas Volume	4.354 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.261 g/L
Nitrogen Produced	1.088 g/L
Nitrogen From N ₂ O	0.000 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:26 AM Last Modified 26-May-1993 9/19/95

Run # 6
Date: 9/18/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	Head Space	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	260 psig
Volume ¹	0.00 /
CO ₂	2.80 %
O ₂	0.00 %
N ₂	5.70 %
CO	0.70 %
N ₂ O	0.00 %
THC	26 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature 2,095 psig

Offgas Volume	4.354 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.327 g/L
Nitrogen Produced	1.241 g/L
Nitrogen From N ₂ O	0.000 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:36 AM Last Modified 26-May-1993 9/19/95

Run # 7
Date: 9/18/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	Head Space	250 ml
Air	N (Y o rN)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	245 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	0.20 %
CO	0.00 %
N ₂ O	0.00 %
THC	<15 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.116 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.041 g/L
Nitrogen From N ₂ O	0.000 g/L

¹Volume measured

²Containing both organic and inorganic carbon

11:50 AM Last Modified 26-May-1993 9/19/95

Run # 8
Date: 9/18/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	245 psig
CO ₂	0.50 %
O ₂	0.00 %
N ₂	1.30 %
CO	0.00 %
N ₂ O	0.10 %
THC	22 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.116 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.044 g/L
Nitrogen Produced	0.268 g/L
Nitrogen From N ₂ O	0.021 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:00 AM Last Modified 26-May-1993 9/27/95

Run #9
Date: 9/18/95
Client: ARMY
Autoclave Material: Ti-11

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	Head Space	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	245 psig
CO ₂	2.40 %
O ₂	0.00 %
N ₂	5.70 %
CO	0.10 %
N ₂ O	0.30 %
THC	37 ppm

Effluent

pH	1.4
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	2,095 psig
Offgas Volume	4.116 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.221 g/L
Nitrogen Produced	1.173 g/L
Nitrogen From N ₂ O	0.062 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:03 AM Last Modified 26-May-1993 9/27/95

Run #10
Date: 9/28/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	Head Space	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.2
Helium	Y (Y o rN)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	ResidenceTime	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	1.40 %
O ₂	0.00 %
N ₂	3.50 %
CO	0.50 %
N ₂ O	0.00 %
THC	87 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1.327 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.171 g/L
Nitrogen Produced	0.734 g/L
Nitrogen From N ₂ O	0.000 g/L

¹Volume measured

²Containing both organic and inorganic carbon

9:57 AM Last Modified 26-May-1993 9/29/95

Run #11
Date: 9/28/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.2
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	2.30 %
O ₂	0.00 %
N ₂	5.20 %
CO	0.00 %
N ₂ O	0.30 %
THC	81 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.207 g/L
Nitrogen Produced	1.091 g/L
Nitrogen From N ₂ O	0.063 g/L

¹Volume measured

²Containing both organic and inorganic carbon

10:03 AM Last Modified 26-May-1993 9/29/95

Run #12
Date: 9/28/95
Client: ARMY
Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.2
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	2.30 %
O ₂	0.00 %
N ₂	5.50 %
CO	0.00 %
N ₂ O	0.40 %
THC	50 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	2,095 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.207 g/L
Nitrogen Produced	1.154 g/L
Nitrogen From N ₂ O	0.084 g/L

¹Volume measured

²Containing both organic and inorganic carbon

10:05 AM Last Modified 26-May-1993 9/29/95

Run #13
Date: 9/20/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.15
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	1.00 %
CO	0.00 %
N ₂ O	6.10 %
THC	<15 ppm

Effluent

pH	2.1
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.210 g/L
Nitrogen From N ₂ O	0.279 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:01 AM Last Modified 26-May-1993 9/21/95

Run #14
Date: 9/20/95
Client: ARMY
Autoclave Material: Ti-11

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.15
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	0.70 %
CO	0.00 %
N ₂ O	5.60 %
THC	<15 ppm

Effluent

pH	2.1
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	1.147 g/L
Nitrogen From N ₂ O	1.175 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:04 AM Last Modified 26-May-1993 9/21/95

Run #15
Date: 9/20/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	245 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.15
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	0.10 %
CO	0.00 %
N ₂ O	5.60 %
THC	<15 ppm

Effluent

pH	1.9
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	2,078 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.116 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.021 g/L
Nitrogen From N ₂ O	1.175 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:06 AM Last Modified 26-May-1993 9/21 Run #11

Run #15a
Date: 9/20/95
Client: ARMY
Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.15
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	0.10 %
CO	0.00 %
N ₂ O	5.90 %
THC	<15 ppm

Effluent

pH	1.9
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.021 g/L
Nitrogen From N ₂ O	1.238 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:08 AM Last Modified 26-May-1993 9/21/95

Run #16

Date: 9/21/95

Client: ARMY

Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	260 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.11
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	245 psig
CO ₂	3.10 %
O ₂	0.00 %
N ₂	1.40 %
CO	0.00 %
N ₂ O	7.80 %
THC	16 ppm

Effluent

pH	1.7
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.116 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.274 g/L
Nitrogen Produced	0.288 g/L
Nitrogen From N ₂ O	1.605 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:05 AM Last Modified 26-May-1993 9/27/95

Run #17
Date: 9/21/95
Client: ARMY
Autoclave Material: Ti-11

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	185 psig
CO ₂	3.60 %
O ₂	0.00 %
N ₂	2.00 %
CO	0.00 %
N ₂ O	8.40 %
THC	15 ppm

Effluent

pH	1.6
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,660 psig
Offgas Volume	3.165 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.244 g/L
Nitrogen Produced	0.316 g/L
Nitrogen From N ₂ O	1.329 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:06 AM Last Modified 26-May-1993 9/27/95

Run #18
Date: 9/21/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	300 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.11
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	300 psig
CO ₂	2.40 %
O ₂	0.00 %
N ₂	1.40 %
CO	0.00 %
N ₂ O	5.90 %
THC	15 ppm

Effluent

pH	1.6
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	2,095 psig
Offgas Volume	4.988 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.257 g/L
Nitrogen Produced	0.349 g/L
Nitrogen From N ₂ O	1.471 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:08 AM Last Modified 26-May-1993 9/27/95

Run #19
Date: 9/21/95
Client: ARMY
Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	1.80 %
O ₂	0.00 %
N ₂	1.40 %
CO	0.00 %
N ₂ O	6.70 %
THC	16 ppm

Effluent

pH	1.5
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,327 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.162 g/L
Nitrogen Produced	0.294 g/L
Nitrogen From N ₂ O	1.405 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:11 AM Last Modified 26-May-1993 9/27/95

Run #20
Date: 9/21/95
Client: ARMY
Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	1.80 %
O ₂	0.00 %
N ₂	0.40 %
CO	0.00 %
N ₂ O	5.40 %
THC	<15 ppm

Effluent

pH	1.5
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.162 g/L
Nitrogen Produced	0.084 g/L
Nitrogen From N ₂ O	1.133 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:16 AM Last Modified 26-May-1993 9/27/95

Run #21
Date: 9/21/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	265 psig
CO ₂	3.00 %
O ₂	0.00 %
N ₂	0.50 %
CO	0.00 %
N ₂ O	7.40 %
THC	<15 ppm

Effluent

pH	1.4
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	2,095 psig
Offgas Volume	4.433 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.285 g/L
Nitrogen Produced	0.111 g/L
Nitrogen From N ₂ O	1.640 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:18 AM Last Modified 26-May-1993 9/27/95

Run #22

Date: 9/28/95

Client: ARMY

Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.2
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	2.10 %
O ₂	0.00 %
N ₂	1.10 %
CO	0.00 %
N ₂ O	6.60 %
THC	31 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.189 g/L
Nitrogen Produced	0.231 g/L
Nitrogen From N ₂ O	1.384 g/L

¹Volume measured

²Containing both organic and inorganic carbon

10:15 AM Last Modified 26-May-1993 9/29/95

Run #23
Date: 9/28/95
Client: ARMY
Autoclave Material: Ti-11

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	280 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.2
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	2.10 %
O ₂	0.00 %
N ₂	1.20 %
CO	0.00 %
N ₂ O	6.40 %
THC	48 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.189 g/L
Nitrogen Produced	0.252 g/L
Nitrogen From N ₂ O	1.342 g/L

¹Volume measured

²Containing both organic and inorganic carbon

10:08 AM Last Modified 26-May-1993 9/29/95

Run #24
Date: 9/28/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	300 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.2
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	260 psig
CO ₂	2.50 %
O ₂	0.00 %
N ₂	1.20 %
CO	0.00 %
N ₂ O	6.20 %
THC	58 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	2,095 psig
Offgas Volume	4.354 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.233 g/L
Nitrogen Produced	0.261 g/L
Nitrogen From N ₂ O	1.350 g/L

¹Volume measured

²Containing both organic and inorganic carbon

10:13 AM Last Modified 26-May-1993 9/29/95

Run #25
Date: 9/21/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	260 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.11
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	250 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	1.80 %
CO	0.00 %
N ₂ O	6.00 %
THC	19 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.196 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.378 g/L
Nitrogen From N ₂ O	1.259 g/L

¹Volume measured

²Containing both organic and inorganic carbon

1:43 PM Last Modified 26-May-1993 9/22/95

Run #26
Date: 9/21/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	260 psig
CO ₂	0.00 %
O ₂	0.00 %
N ₂	1.50 %
CO	0.00 %
N ₂ O	6.60 %
THC	<15 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,660 psig
Offgas Volume	4.354 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.327 g/L
Nitrogen From N ₂ O	1.437 g/L

¹Volume measured

²Containing both organic and inorganic carbon

1:45 pM Last Modified 26-May-1993 9/22/95

Run #27
Date: 9/22/95
Client: ARMY
Autoclave Material: Ti-11

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	260 psig
CO ₂	0.00 %
O ₂	0.20 %
N ₂	2.40 %
CO	0.00 %
N ₂ O	7.10 %
THC	<15 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	2,095 psig
Offgas Volume	4.354 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.000 g/L
Nitrogen Produced	0.522 g/L
Nitrogen From N ₂ O	1.546 g/L

¹Volume measured

²Containing both organic and inorganic carbon

1:48 AM Last Modified 26-May-1993 9/22/95

Run #28
Date: 9/22/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	260 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.11
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	275 psig
CO ₂	5.10 %
O ₂	0.00 %
N ₂	5.40 %
CO	0.00 %
N ₂ O	6.60 %
THC	<15 ppm

Effluent

pH	1.6
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	1,327 psig
Offgas Volume	4.592 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.502 g/L
Nitrogen Produced	1.240 g/L
Nitrogen From N ₂ O	1.515 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:19 AM Last Modified 26-May-1993 9/27/95

Run #29
Date: 9/22/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	280 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.11
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	300 psig
CO ₂	5.40 %
O ₂	0.00 %
N ₂	6.80 %
CO	0.00 %
N ₂ O	6.40 %
THC	<15 ppm

Effluent

pH	1.4
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.988 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.577 g/L
Nitrogen Produced	1.696 g/L
Nitrogen From N ₂ O	1.596 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:21 AM Last Modified 26-May-1993 9/27/95

Run #30
Date: 9/22/95
Client: ARMY
Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	285 psig
CO ₂	5.00 %
O ₂	0.00 %
N ₂	5.90 %
CO	0.00 %
N ₂ O	6.00 %
THC	<15 ppm

Effluent

pH	1.5
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume

Pressure @ Temperature	2,095 psig
Offgas Volume	4.750 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.509 g/L
Nitrogen Produced	1.401 g/L
Nitrogen From N ₂ O	1.425 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:22 AM Last Modified 26-May-1993 9/27/95

Run #31
Date: 9/25/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	270 psig
CO ₂	3.50 %
O ₂	0.00 %
N ₂	6.60 %
CO	0.00 %
N ₂ O	5.20 %
THC	16 ppm

Effluent

pH	1.4
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,327 psig
Offgas Volume	4.513 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.339 g/L
Nitrogen Produced	1.489 g/L
Nitrogen From N ₂ O	1.173 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:25 AM Last Modified 26-May-1993 9/27/95

Run #32
Date: 9/25/95
Client: ARMY
Autoclave Material: Ti-9

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	280 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	275 psig
CO ₂	3.60 %
O ₂	0.00 %
N ₂	6.10 %
CO	0.30 %
N ₂ O	5.60 %
THC	20 ppm

Effluent

pH	1.4
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.592 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.384 g/L
Nitrogen Produced	1.400 g/L
Nitrogen From N ₂ O	1.286 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:27 AM Last Modified 26-May-1993 9/27/95

Run #33
Date: 9/25/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.11
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	300 psig
CO ₂	4.60 %
O ₂	0.00 %
N ₂	6.80 %
CO	0.00 %
N ₂ O	5.90 %
THC	33 ppm

Effluent

pH	1.4
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	2,095 psig
Offgas Volume	4.988 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.492 g/L
Nitrogen Produced	1.696 g/L
Nitrogen From N ₂ O	1.471 g/L

¹Volume measured

²Containing both organic and inorganic carbon

8:28 AM Last Modified 26-May-1993 9/27/95

Run #34
Date: 9/29/95
Client: ARMY
Autoclave Material: Ti-11

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.2
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	260 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	265 psig
CO ₂	2.50 %
O ₂	0.00 %
N ₂	5.90 %
CO	0.00 %
N ₂ O	5.80 %
THC	22 ppm

Effluent

pH	1.2
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,327 psig
Offgas Volume	4.433 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.238 g/L
Nitrogen Produced	1.308 g/L
Nitrogen From N ₂ O	1.286 g/L

¹Volume measured

²Containing both organic and inorganic carbon

1:40 PM Last Modified 26-May-1993 9/29/95

Run #35
Date: 9/29/95
Client: ARMY
Autoclave Material: Ti-17

Initial Charge Condition

Temperature	20 °C
Pressure	250 psig
Air	N (Y or N)
Oxygen	N (Y or N)
Helium	Y (Y or N)
Set Point Temperature	280 °C

Liquid Volume	250 ml
HeadSpace	250 ml
Chemical Oxygen Demand	20 g/L
pH	1.2
Barometric Pressure	730 mm Hg
Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	275 psig
CO ₂	2.70 %
O ₂	0.00 %
N ₂	6.70 %
CO	0.00 %
N ₂ O	5.80 %
THC	18 ppm

Effluent

pH	1.1
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	1,660 psig
Offgas Volume	4.592 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.266 g/L
Nitrogen Produced	1.538 g/L
Nitrogen From N ₂ O	1.331 g/L

¹Volume measured

²Containing both organic and inorganic carbon

1:28 AM Last Modified 26-May-1993 9/29/95

Run #36
Date: 9/29/95
Client: ARMY
Autoclave Material: Ti-3

Initial Charge Condition

Temperature	20 °C	Liquid Volume	250 ml
Pressure	250 psig	HeadSpace	250 ml
Air	N (Y or N)	Chemical Oxygen Demand	20 g/L
Oxygen	N (Y or N)	pH	1.2
Helium	Y (Y or N)	Barometric Pressure	730 mm Hg
Set Point Temperature	300 °C	Residence Time	60 minutes

Offgas Analysis

Temperature	20 °C
Pressure	280 psig
CO ₂	2.80 %
O ₂	0.00 %
N ₂	6.10 %
CO	0.00 %
N ₂ O	6.20 %
THC	22 ppm

Effluent

pH	1.3
Liquid Volume	250 ml

Calculation Results

Using Calculated Volume	
Pressure @ Temperature	2,095 psig
Offgas Volume	4.671 Std liters
Input Gas Volume	4.196 Std liters
Carbon Reacted ²	0.280 g/L
Nitrogen Produced	1.425 g/L
Nitrogen From N ₂ O	1.448 g/L

¹Volume measured

²Containing both organic and inorganic carbon

1:30 PM Last Modified 26-May-1993 9/29/95

Appendix C: WAO of RAAP Sludge — Final Water Quality Data

Sample	Sludge volume (mL)	Ammonium nitrate volume (mL)	Ammonium nitrate concentration (g/L)	Final set temperature (C)	Final pressure (psi)	COD mg/L	TSS mg/L
WAO 97-09	150	100	100	10	—	8,980	5,300
WAO 97-07	150	100	100	280	901	5,740	1,290
WAO 97-13	150	100	100	300	1,230	5,690	505
WAO 97-06	150	100	100	325	1,850	456	585
WAO 97-10	170	80	100	10	—	10,100	6,050
WAO 97-12	170	80	100	280	910	6,590	1,530
WAO 97-15	170	80	100	300	1,248	6,450	1,610
WAO 97-08	170	80	100	325	1,850	2,450	1,080
WAO 97-11	190	60	100	10	—	9,830	5,690
WAO 97-05	190	60	100	280	910	7,610	1,800
WAO 97-14	190	60	100	300	1,225	6,760	1,140
WAO 97-04a	190	60	100	325	1,799	5,730	1,980
WAO 97-04	250	—	—	280	916	10,900	1,940
WAO 97-03	250	—	—	325	1,755	9,870	1,290
WAO 97-01	250	—	—	—	—	10,500	8,830
WAO 97-02	250	—	—	—	—	14,300	9,310

Sample	SVI	Ammonia mg/L-N	Nitrate mg/L-N	TOC µgC/g	BOD mg/L	TKN mg/L-N
WAO 97-09	100	7,760	7,040	2,040	2,920	5,620
WAO 97-07	6.3	7,670	6,510	903	2,970	5,930
WAO 97-13	4.1	7,490	5,590	390	2,340	5,250
WAO 97-06	7.1	2,180	1,450	117	350	1,760
WAO 97-10	99	6,230	5,610	2,320	3,060	5,060
WAO 97-12	11	6,690	4,920	1,070	3,440	4,160
WAO 97-15	7.6	5,940	4,230	993	4,410	4,500
WAO 97-08	3.8	1,960	1,000	332	1,470	1,670
WAO 97-11	120	3,760	4,110	2,200	3,290	3,790
WAO 97-05	9.1	4,450	3,510	1,100	3,500	2,250
WAO 97-14	14	4,370	2,890	984	3,710	3,330
WAO 97-04a	4.2	2,230	761	744	3,040	1,990
WAO 97-04	4.2	682	13	1,600	3,500	850
WAO 97-03	6.3	698	3.99	1,160	3,500	770
WAO 97-01	100	298	0.035	3,340	3,000	890
WAO 97-02	44	292	0.044	3,320	5,200	820

Distribution

Chief of Engineers

ATTN: CEHEC-IM-LH (2)
ATTN: HECSA Mailroom (2)
ATTN: CECC-R
ATTN: CERD-L
ATTN: CERD-M

Industrial Operations Command

ATTN: AMSIO-EQC

US Army Materiel Command (AMC) Installations:

Rock Island, IL 61299-7190

ATTN: AMXEN-C

Radford Army Ammunition Plant 24141

ATTN: SMCRA-EN

Aberdeen Proving Ground 21005

ATTN: STEAP-FE

Rock Island Arsenal 61299

ATTN: SMCRI-PW

Harry Diamond Lab

ATTN: Library 20783

Picatinny Arsenal 07806

ATTN: AMSTA-AR-IMC

US Army Materials Tech Lab

ATTN: SLCMT-DPW 02172

US Army Environmental Center

ATTN: SFIM-AEC-ET 21010

ATTN: SFIM-AEC-CR 64152

ATTN: SFIM-AEC-SR 30335-6801

ATTN: AFIM-AEC-WR 80022-2108

Defense Tech Info Center 22304

ATTN: DTIC-O (2)

21

8/99

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE September 1999	3. REPORT TYPE AND DATES COVERED Final	
4. TITLE AND SUBTITLE Reuse of Ammonium Nitrate: Wet Air Oxidation			5. FUNDING NUMBERS D048 T77	
6. AUTHOR(S) Stephen W. Maloney				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Construction Engineering Research Laboratory (CERL) P.O. Box 9005 Champaign, IL 61826-9005			8. PERFORMING ORGANIZATION REPORT NUMBER TR 99/74	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Environmental Center SFIM-AEC-ET Aberdeen Proving Ground, MD 21010			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SUPPLEMENTARY NOTES Copies are available from the Defense Technical Information Center, 8725 John J. Kingman Road, Suite 0944, Fort Belvoir, VA 22060-6218.				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Ammonium nitrate (AN) is a possible replacement for ammonium perchlorate as an oxidizer in solid rocket motors potentially generating large amounts of AN to be recycled or reused. AN requires phase stabilization before it can be used, so small amounts of potassium dinitrimide (KDN) are added to create phase stabilized ammonium nitrate (PSAN). Reuse alternatives would either require separating the KDN or destroying it. AN is commonly used as a fertilizer (80 percent of AN produced) and an oxidizer. Owing to the high demand and wide availability of AN for its most common use, the commercial cost is very low. This precludes reuse alternatives, which would require separation of the KDN. So, this report focused on destructive reuse as an oxidizer in wet air oxidation (WAO). The PSAN was tested to see if KDN was destroyed during WAO, and AN was tested as an oxidizer in WAO treatment of an Army hazardous waste sludge. WAO will degrade KDN, and PSAN can be effectively used as an oxidizing agent. The hazardous waste sludge could be treated effectively. Sludge volume index was significantly reduced, meaning that the amount of sludge requiring disposal would be greatly reduced, offsetting the cost of WAO.				
14. SUBJECT TERMS sludge disposal hazardous wastes wet air oxidation (WAO) ammonium nitrate			15. NUMBER OF PAGES 98	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR	